

**Appendix I**

**Reactivity: MSE Drum Tests**



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## **Appendix I**

### **Reactivity: MSE Drum Tests**

In situ thermal desorption (ISTD) is being investigated as a treatment option for transuranic (TRU)-contaminated buried waste at the Idaho National Laboratory (INL) Site. The ISTD treatment envisioned for this waste places relatively low-power insertion heaters in a grid pattern throughout the Subsurface Disposal Area (SDA) treatment area. The insertion heaters, rated at 91.4 W/m (300 W/ft) of rod length, are enclosed in a perforated, 15.2-cm (6-in.)-diameter steel casing. Each of these heater assemblies is sealed at the treatment area surface so that a slight vacuum applied at the head of individual heater assemblies draws desorbed or thermally decomposed waste constituents and soil air and moisture through the heater assembly into an off-gas treatment system. The heater assemblies have a maximum operating temperature of 871°C (1,600°F). Actual temperature within the perforated casing is expected to be approximately 593°C (1,100°F), with temperature in the surrounding waste or soil ranging downward from 399°C (750°F), depending on distance from heater assembly and length of time heat is applied. In practice, heat will be applied until all the surrounding waste or soil is 104°C (220°F) or greater, with temperature at 15.2 cm (6 in.) from heater assembly expected to reach up to approximately 450°C (842°F).

To assess whether these ISTD heater assemblies could be used at the SDA, the technology was tested at drum scale. The work was conducted by MSE Technology Applications, Inc., under the direction of Bechtel BWXT Idaho, LLC.

#### **I-1. TEST OBJECTIVES, RATIONALE, AND DEVIATIONS FROM TEST PLAN**

The objective of the work described in this report is to assess the effectiveness of ISTD for treatment of waste buried in the SDA at the INL Site, particularly with regard to questions of waste reactivity, off-gas composition, contaminant destruction and removal efficiency, and actinide fixation. The test uses a drum-scale test bed and involves the following:

- Formulating and preparing simulated nitrate sludge, organic sludge, and debris mixtures
- Heating 55-gal drum quantities of various combinations of these materials and soil from the INL Site
- Determining the composition of pretest and posttest feed samples and off-gases
- Assessing the contaminant destruction and removal efficiency of ISTD treatment
- Assessing off-gas treatment needs for ISTD of waste buried in the SDA.

Data generated during these tests support modeling of contaminant transport from the treated waste form. The tests have application with TRU pits and trenches, non-TRU pits and trenches, and soil vault rows.

#### **I-2. EXPERIMENTAL DESIGN AND PROCEDURES**

The MSE vacuum thermal desorption system consists of a carbon-steel chamber sized to completely enclose a 55-gal test drum. The test chamber was designed mechanically to withstand internal

pressures from 0 to 1.5 atm (i.e., to withstand an internal high vacuum or an overpressure of 0.5 atm). For these tests, the system was operated under a slight vacuum (10.2–12.7 cm [4–5 in.] of water). The slight vacuum primarily was intended to simulate ISTD heating but also ensured that any gases released in the drum during thermal desorption were drawn into the off-gas treatment system, preventing leakage into the work area around the test bed.

The drum-and-chamber vacuum is controlled by monitoring chamber pressure and regulating the motive gas through an eductor with a control valve. The eductor draws purge and process gas from the chamber and the 55-gal test drum, respectively, to equalize the pressure between them. Process gases released during thermal desorption of the 55-gal test drum are drawn through the insertion heater assembly and past several sampling ports before mixing with the purge gas drawn from the chamber, as shown in Figure I-1.

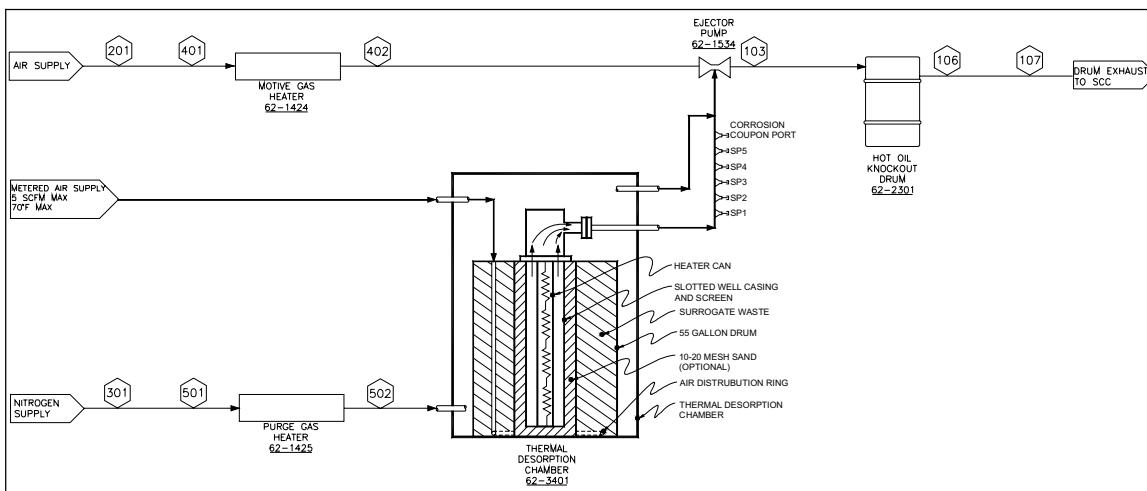


Figure I-1. Process schematic of MSE vacuum thermal desorption system.

To simulate airflow through soil into the slight vacuum of an ISTD heater assembly, air is metered by a mass flow control valve into the bottom of the 55-gal test drum where the air can be dispersed circumferentially around the drum by a distribution ring or injected at a point near the bottom of the drum. The air distribution ring and other components are shown in Figure I-1 and in somewhat greater detail in Figure I-2.

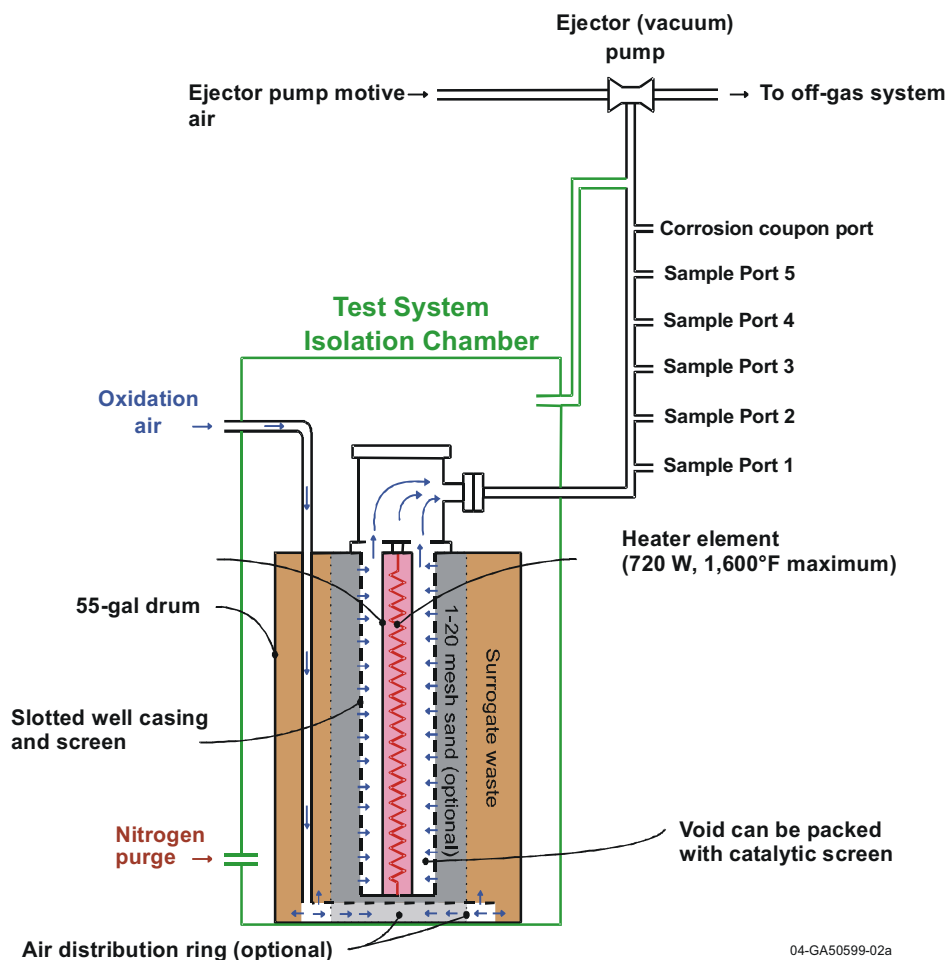


Figure I-2. Schematic of barrel portion of the MSE barrel thermal desorption system.

For Drum 3 (the organic sludge and combustible debris test) and Drum 4 (the organic sludge and combustible debris soil test), the air distribution ring was removed, and air was injected at a single point near the bottom of the drum. Additionally, for Drum 3, a corrosion-resistant metal screen was wrapped five times around the heater can to provide additional reactive surfaces in the void between the slotted well casing and the heater can. Photographs of the test system are shown in Figures I-3 and I-4. In Figure I-4, the drums were placed in the test chamber at the right-hand end of the skid. The individual sampling lines of Figure I-1 are not shown in this photograph. The mechanical pump partly shown in the foreground was not used; a valve turned it off. Barrel thermal desorption system components are listed in Table I-1.

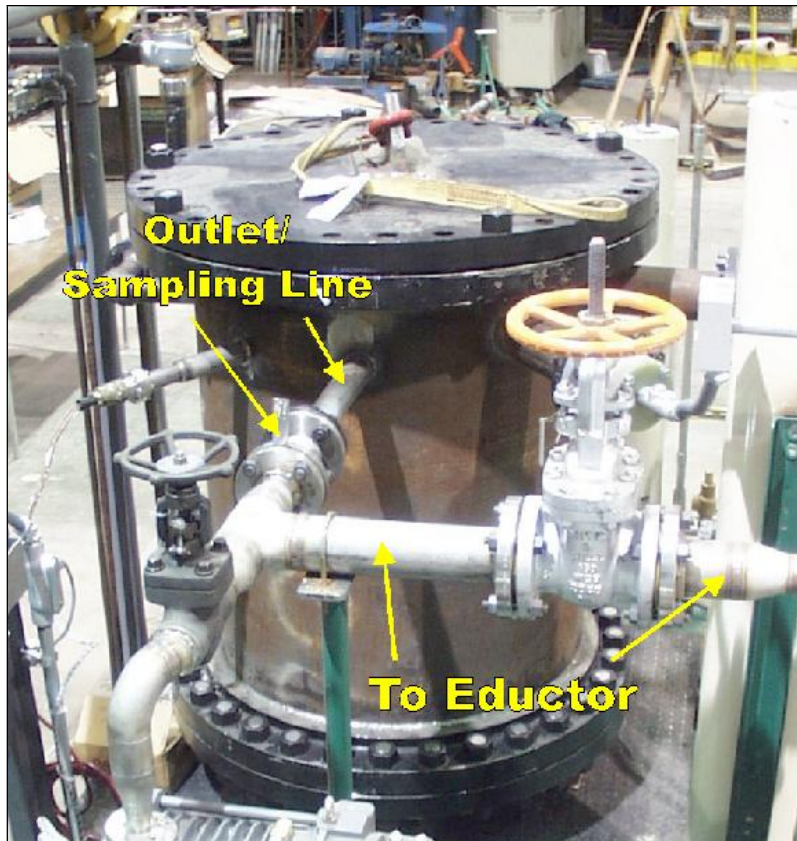


Figure I-3. Photograph of test chamber for vacuum thermal desorption showing the outlet/sampling line.

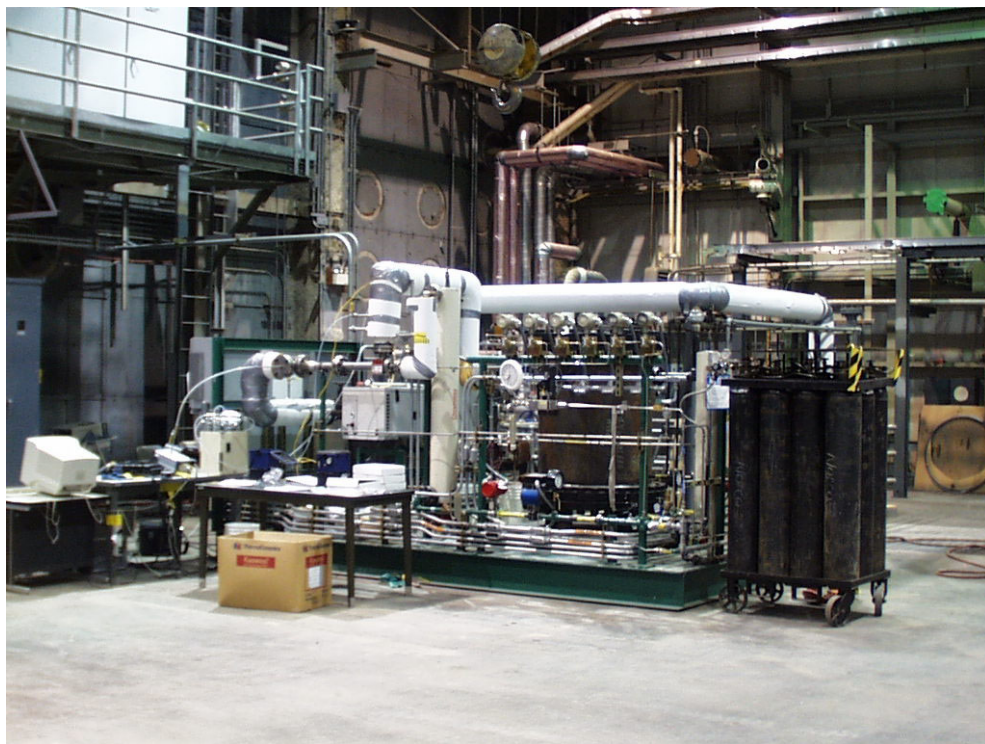


Figure I-4. Photograph of equipment used for drum testing.

Table I-1. Descriptions of components of vacuum thermal desorption system.

Input/Output and Components (Schematic Identification Number)	Description
Test cell (62-3401)	
Test cell tubular heater	TerraTherm, 300 W/ft, 871°C (1,600°F) maximum temperature.
Test cell weigh scale (62-3801)	
Motive gas heater (62-1424)	Heater for eductor motive gas: 26 kW, 399°C (750°F) maximum temperature, depending on flow rate.
Purge gas heater (62-1425)	Heater for test cell purge gas: 8 kW, 399°C (750°F) maximum temperature, depending on flow rate.
Ejector (eductor) pump (62-1534)	Venturi effect eductor pump, Croll-Reynolds Clean Air Technologies Model #2Z, ejector can handle 59 lb/hour (13 scfm) of air at 2.9 psia and 399°C (750°F) while discharging to 13.3 psia using 391 lb/hour (87 scfm) of motive air at 122.8 psia and 399°C (750°F).
Hot-oil knockout drum (62-2301)	Carbon steel construction.
Insertion point for pitot tube (SP-1)	A straight stem pitot tube was mounted through a compression fitting in the drum outlet line between the drum and the eductor vacuum pump. Pressure was measured with a Testo analyzer. The pitot tube was mounted upstream of other sampling lines.
Sampling point for Testo analyzer (SP-2)	The Testo gas sampling probe was mounted through a compression fitting in the drum outlet line between the drum and the eductor vacuum pump. The Testo analyzer included a vacuum pump; no other motive force was required for sampling by the Testo analyzer.
Sampling line for particulate monitor (SP-3)	A 1/4-in. 316 stainless steel sampling line directed sample gas to an aerosol monitor (ThermoAnderson Model DR-4000). The sampling line was connected to the drum outlet line through a compression fitting, with the line mounted so that the opening faced upstream in the duct. Sampling was nonisokinetic. The ThermoAnderson aerosol monitor included a pump; no other motive force was needed for this sampling line.
Sampling line for Tedlar bag samples for volatile organic compounds and hydrochloric acid/chlorine analysis (SP-4)	A 1/4-in. 316 stainless steel sampling line was mounted, through a compression fitting, in the drum outlet line between the drum and the eductor vacuum pump. This line was used to take Tedlar bag samples—for volatile organic compound and hydrochloric acid/chlorine analysis—using a vacuum box; no other motive force was needed for this sampling line.
Sampling line for continuous oxygen monitor (SP-5)	A 1/4-in. 316 stainless steel line was mounted through a compression fitting to the drum outlet line between the drum and the ejector vacuum pump. The sampling flow was directed to a continuous oxygen analyzer (Illinois Instruments Model 6000).
Identifiers correspond to those shown in Figure I-1.	

Six thermocouples monitored the temperature of the drum contents during heating. The thermocouples are installed in three stainless steel tubes with one thermocouple near the top and one thermocouple near the bottom of each tube. These tubes are inserted vertically into the drum feed material with one tube inserted near the center heater assembly, one tube inserted halfway between the heater

assembly and the drum wall and one tube inserted near the drum wall. The thermocouples are identified by position as top or bottom, and inner, middle, or outer.

### **I-3. EQUIPMENT AND MATERIALS**

The surrogate material had five tests: shakedown, organic sludge surrogate (Drum 1), nitrate salt surrogate (Drum 2), organic sludge with combustible debris surrogate (Drum 3), and organic sludge with combustible debris and soil surrogate (Drum 4). Planned test durations were 5 days or less. Electrical power was applied to the heater assembly on the first day of testing as soon as the test system could be brought to readiness and continued until a preselected target temperature was reached, to a maximum of 8 days, leaving 1 day for cooling and securing the system.

The following sections describe each of the five tests.

#### **I-3.1 Shakedown Test**

The objective of the shakedown test was to check out system components and to monitor the heating profile of the drum contents. The drum contents were a mixture of soil from the INL Site, kitty litter, Microcel E, and water, formulated to simulate the heat capacity, heat of vaporization, and total gas generation of the organic sludge. By using relatively inert constituents, a comparison of the shakedown test to the later organic sludge test (Drum 1) was expected to reveal any heating effects because of organic sludge chemical reactions. The shakedown feed formulation is shown in Table I-2.

Table I-2. Formula for shakedown soil-water surrogate.

Shakedown Surrogate	Total Required (kg)	Percent (wt%)
Soil from the INL Site	101.0	53.2
Water	16.6	8.8
Microcel E	46.9	24.7
Kitty litter	25.3	13.3
Total	189.8	100.0

The shakedown feed material was loaded into a 55-gal drum, which was then placed in the main test chamber of the barrel thermal desorption skid. For the shakedown test, electrical power was applied to the heater assembly for 65 hours. Nominal airflow into the test drum was 0.5 lb/minute.

#### **I-3.2 Organic Sludge Test (Drum 1)**

The organic sludge surrogate was a mixture of cutting oil, halogenated solvents, and adsorbents, as shown in Table I-3. All organic liquids in this surrogate have fuel value; therefore, this mixture had the potential to react with injected air and produce heat. This combustion process, if it occurred, was expected to take place either within the heater assembly or in the hottest portion of feed material near the heater assembly. For the organic sludge test, electrical power was applied to the heater assembly for 22 hours. Nominal airflow into the test drum was 0.5 lb/minute.

Table I-3. Formula for organic sludge surrogate (Drum 1).

Organic Sludge Surrogate		Required Percent (wt%)
Liquids:		
Machine oil	Texaco Regal Oil	28
Carbon tetrachloride	CCl <sub>4</sub>	27
1,1,1-trichlorethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	9
Trichloroethene	C <sub>2</sub> HCl <sub>3</sub>	7
Tetrachloroethene	C <sub>2</sub> Cl <sub>4</sub>	7
Subtotal		78
Solids:		
Microcel E	Silicon oxide	13
Kitty litter	Oil Dri	7
Ceric oxide	CeO <sub>2</sub>	2
Subtotal		22
Total		100

### I-3.3 Nitrate Salt Test (Drum 2)

The nitrate salt surrogate was a mixture of 90% nitrate salts, miscellaneous other salts, 1% ethylenediaminetetraacetic acid (EDTA), and 0.5% ceric oxide (added as a plutonium surrogate), as shown in Table I-4. (The as-mixed formula was normalized to a total of 100%.) For the nitrate salt test, electrical power was applied to the heater assembly for 65 hours. Nominal airflow into the test drum was 0.5 lb/minute.

Table I-4. Formula for nitrate salt surrogate (Drum 2).

Nitrate Salt Surrogate		Required Percent (wt%)
Sodium nitrate	NaNO <sub>3</sub>	60.0
Potassium nitrate	KNO <sub>3</sub>	30.0
Sodium sulfate	Na <sub>2</sub> SO <sub>4</sub>	3.0
Sodium chloride	NaCl	3.0
Disodium hydrogen phosphate heptahydrate	Na <sub>2</sub> HPO <sub>4</sub> ·7H <sub>2</sub> O	1.0
Sodium bicarbonate	NaHCO <sub>3</sub>	0.5
Sodium fluoride	NaF	0.5
Sodium nitrite	NaNO <sub>2</sub>	1.0
EDTA	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub>	1.0
Ceric oxide	CeO <sub>2</sub>	0.5
Total		100.5

### I-3.4 Organic Sludge with Combustible Debris Test (Drum 3)

A combustible debris surrogate consisting of 40 wt% cotton rags, 40 wt% paper towels, 10 wt% polyethylene beads, 5 wt% polyvinyl chloride (PVC) beads, and 5 wt% acrylonitrile-butadiene-styrenes (ABS) plastic beads was prepared for this test (see Table I-5). The combustible debris surrogate was intended to simulate combustible laboratory trash from Rocky Flats Plant. The feed formulation for this test consisted of 35 wt% organic sludge, 55 wt% combustible debris, and 10 wt% water. This formulation was intended to simulate the contents of drums buried at the Radioactive Waste Management Complex that contain cutting oil, halogenated solvents, adsorbents, paper, cloth, and plastic scrap. For the organic sludge with combustible debris test (Drum 3), electrical power was applied to the heater assembly for 50.1 hours. Nominal airflow to the test drum was 0.5 lb/minute.

Table I-5. Formula for organic sludge surrogate and combustible debris surrogate (Drum 3).

Organic Sludge Surrogate (35 wt% of mix)		Required Percent (wt%)
Liquids:		
Machine oil	Texaco Regal Oil	28
Carbon tetrachloride	CCl <sub>4</sub>	27
1,1,1-trichlorethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	9
Trichloroethene	C <sub>2</sub> HCl <sub>3</sub>	7
Tetrachloroethene	C <sub>2</sub> Cl <sub>4</sub>	7
Subtotal		78
Solids:		
Microcel E	Silicon oxide	13
Kitty litter	Oil Dri	7
Ceric oxide	CeO <sub>2</sub>	2
Subtotal		22
Combustible Debris Surrogate (55 wt% of mix)		Required Percent (wt%)
Rags		40
Paper towels		40
Polyethylene		10
ABS plastic		5
PVC plastic		5
Water (10 wt% of mix)		Required Percent (wt%)
Water	H <sub>2</sub> O	100

### I-3.5 Organic Sludge with Combustible Debris and Soil Test (Drum 4)

A soil surrogate—containing a tracer—consisting of 83 wt% soil from the INL Site, 15 wt% water, and 2 wt% ceric oxide was prepared for this test as shown in Table I-6. The soil surrogate was intended to simulate the soil covering the buried waste in the SDA. The feed formulation for this test consisted of 40 wt% organic sludge, 30 wt% tracer containing soil, and 30 wt% combustible debris. This formula simulated the contents of drums buried at the Radioactive Waste Management Complex mixed with soil from the INL Site. For the organic sludge with combustible debris and soil test (Drum 4), electrical power was applied to the heater assembly for 167 hours. Nominal airflow to the test drum was 0.5 lb/minute.

Table I-6. Formula for organic sludge with combustible debris and soil surrogate (Drum 4).

Organic Sludge Surrogate (40 wt% of mix)		Required Percent (wt%)
Liquids:		
Machine oil	Texaco Regal Oil	28
Carbon tetrachloride	CCL <sub>4</sub>	27
1,1,1-trichlorethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	9
Trichloroethene	C <sub>2</sub> HCl <sub>3</sub>	7
Tetrachloroethene	C <sub>2</sub> Cl <sub>4</sub>	7
Subtotal		78
Solids:		
Microcel E	Silicon oxide	13
Kitty litter	Oil Dri	7
Ceric oxide	CeO <sub>2</sub>	2
Subtotal		22
Soil Containing Tracer (30 wt% of mix)		Required Percent (wt%)
Soil from the INL Site		83
Water	H <sub>2</sub> O	15
Ceric oxide	CeO <sub>2</sub>	2
Combustible Debris (30 wt% of mix)		Required Percent (wt%)
Rags		40
Paper towels		40
Polyethylene		10
ABS plastic		5
PVC plastic		5

## I-4. DATA MANAGEMENT, ANALYSIS, AND INTERPRETATION

Because the temperature of the drum contents determined volatilization and pyrolysis of drum contents, the primary variable of interest for the ISTD drum tests was the temperature of the drum contents as a function of time. Temperatures of the drum contents for the shakedown, organic sludge, nitrate salt, and organic with combustibles tests are shown in Figure I-5. The legend for Figure I-5 indicates the test and thermocouple locations as follows:

- The first two or three characters indicate the test: shakedown (Shk), organic sludge (Org), nitrate salt (Nit), organics with combustibles (D3), or organics with combustibles and soil (D4)
- The middle character indicates the thermocouple identifier
- The last two characters indicate the thermocouple locations, which were inner bottom (IB), inner top (IT), midbottom (MB), midtop (MT), outer bottom (OB), and outer top (OT).

As shown in the legend for Figure I-5, each line color in the graph indicates a particular test (e.g., green indicates the nitrate salt test (Drum 2)). See system description for a discussion of thermocouple locations.

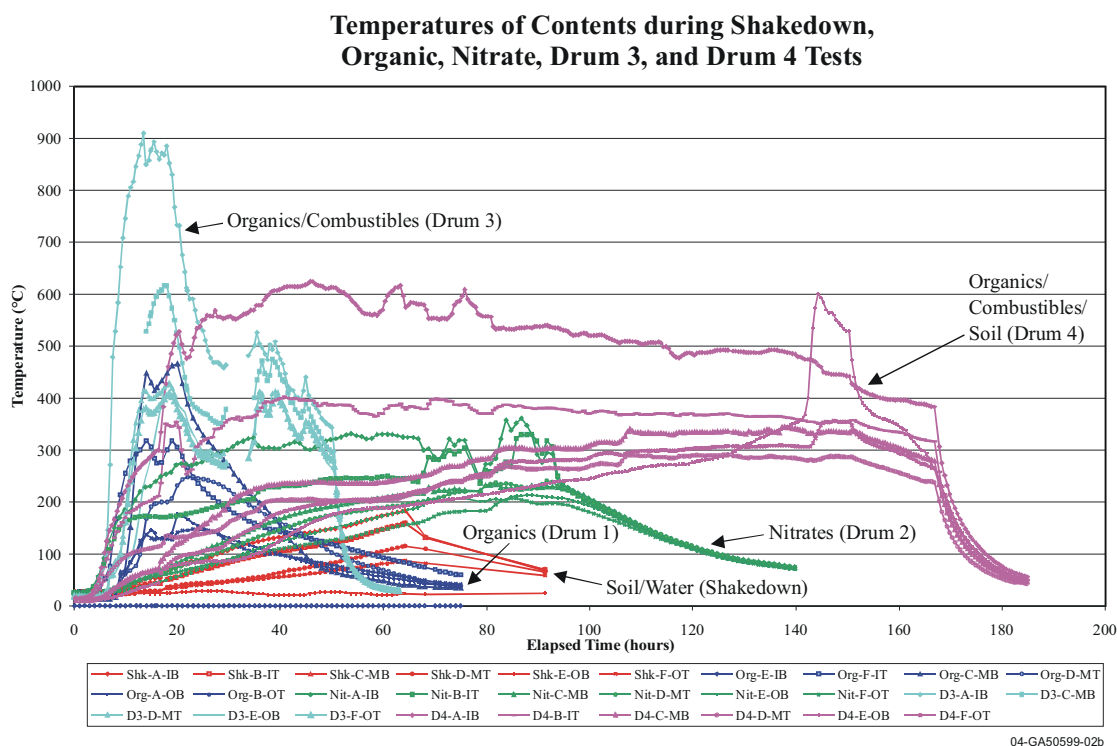


Figure I-5. Temperatures of test drum contents.

Air was injected near the bottom of the drum. The injected air was expected to flow (1) through the feed material near the heater assembly, (2) through the perforated casing surrounding the heater assembly, (3) into the heater assembly, (4) out of the top of the heater assembly, and (5) into the outlet and sampling lines leading to the eductor and the off-gas treatment system. Temperatures were expected to rise gradually from the central heater assembly outward to the walls of the drum.

As shown in Figure I-5, heating rates and the maximum temperatures varied substantially from test to test. Factors affecting heating rate were assumed to be power input to the heater, water content in the feed material, airflow into the drum, and fuel value of material volatilizing from the feed. In principle, heater power input would have been held constant at 720 W. In practice, the heater target temperature was set, and the heater thermostat then automatically varied the power input, between zero and 720 W, to eventually reach and then maintain the target heater temperature. For the shakedown test, power input was generally at the maximum (720 W), and even then, the temperature of the drum contents rose relatively slowly. For the tests of organic sludge (D1), organics with combustibles (D2), and organics with combustibles and soil (D4), after a period of initial heatup, the drum contents began self-heating, and the heater controller automatically reduced the electrical power input, sometimes to zero.

These and other factors affecting heating rates for specific tests are discussed below.

#### **I-4.1 Shakedown and Organic Sludge Tests**

The shakedown test feed material was formulated to simulate the heat capacity and heat of vaporization of the organic sludge feed. As shown in Figure I-5, the peak temperature achieved for the shakedown test was approximately 180°C (356°F) after 65 hours of heating. The organic sludge feed was expected to give the same temperature profile, unless combustion of the organics or some other effect altered the heating rate. However, during the organic sludge test (Drum 1), the drum contents reached a peak temperature of approximately 468°C (874.4°F) after 20 hours of heating, indicating a significantly accelerated heating rate relative to the shakedown feed, apparently caused by combustion of volatile organics in the organic sludge feed.

Off-gas from the organic sludge test was sampled and analyzed for hydrogen chloride and chlorine gas and the four volatile organic compounds (VOCs) included in the drum contents. As shown in Figure I-6, the peak hydrogen chloride concentration, approximately 33 vol%, was reached 22 hours from the start of the test. Up to that time, there were no detectable feed VOCs in the off-gas. At 18 hours, when the drum contents near the drum wall exceeded the target temperature of 105°C (221°F), the heater assembly was powered down. At 19 hours, combustion air to the drum was discontinued. Shortly after, at 22 hours, the temperature of the drum contents began to decline, off-gas hydrogen chloride concentrations abruptly dropped off, and off-gas VOC concentrations abruptly increased. The VOC concentrations peaked at about 32 hours from the start of the test. At 35 hours, a nitrogen purge of the drum was started, which resulted in a dilution of the off-gas organics, as reflected in Figure I-6.

The crossover of hydrogen chloride and VOC concentrations apparently was due to incomplete combustion of VOCs volatilized from the feed material. While power was supplied to the heater, the VOCs, which were the only source of chlorine, were evidently fully oxidized to hydrogen chloride, carbon dioxide, and water. When the heater power was turned off, the VOCs continued to volatilize from the drum; however, the presumed combustion zone near or within the heater assembly was apparently no longer hot enough to oxidize the VOCs. A qualitative organic compound scan of an off-gas sample taken during this cooling period showed numerous partially dechlorinated products of the feed organic VOCs, further suggesting incomplete oxidation of organics after the heater power was turned off.

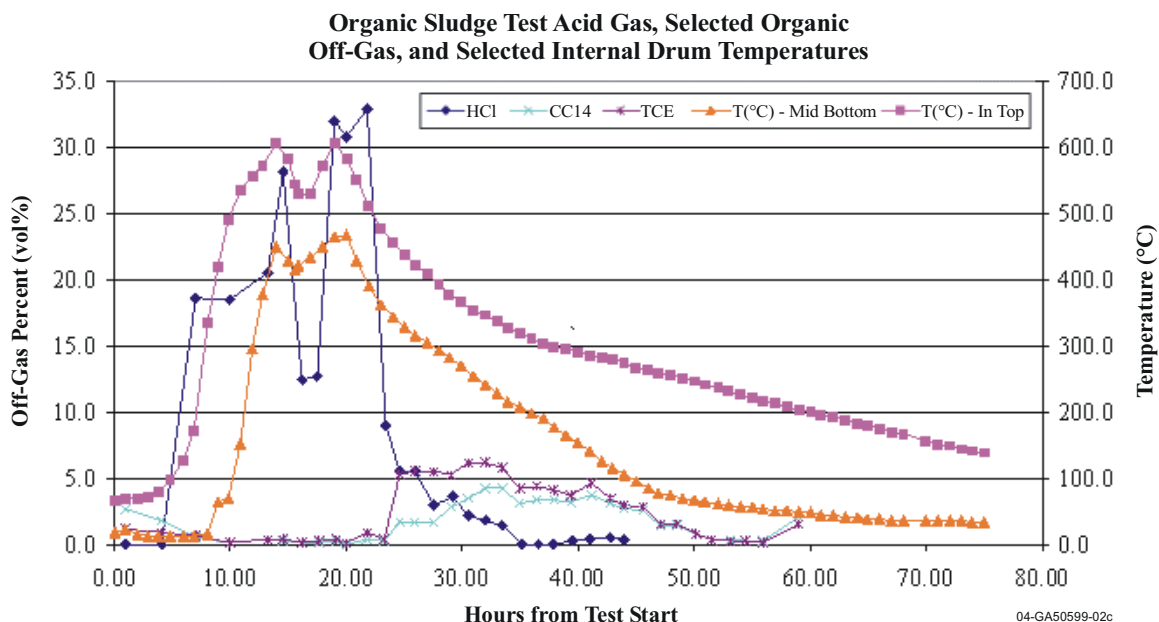


Figure I-6. Generation of acid gas in organic sludge test, selected off-gas volatile organics, and selected internal drum temperatures (Drum 1).

The MSE concluded that the heater assembly performed as expected (i.e., when power was applied, VOCs in the drum were gradually volatilized and oxidized with generation of heat). When the heater power was turned off, the VOCs continued to volatilize as the drum cooled; however, they were no longer being fully oxidized. Volatilization of VOCs gradually dropped off as the drum cooled. An additional result, as expected from the pretest safety analysis, was that a feed containing combustible organics, but no oxidizers, could be safely processed in the drum test system.

Analysis of posttest drum solids showed residual concentrations up to 0.2 wt% of the four feed VOCs, indicating that the VOCs had been mostly, but not completely, volatilized. Figures I-7 and I-8 show photographs of the contents of the drum after the heating process was completed and the drum had cooled.



Figure I-7. Final drum contents from test of mixture of organic sludge surrogate.



Figure I-8. Final drum contents from test of mixture of organic sludge surrogate.

## I-4.2 Nitrate Salt Test (Drum 2)

The objective of the nitrate salt test was to simulate, at drum scale, ISTD treatment of a nitrate salt surrogate mixture while monitoring heating rates, apparent reactivity, and generation of off-gas for the mixture.

As shown in Table I-4, the nitrate salt feed consisted of a mixture of inorganic salts, primarily sodium nitrate (60 wt%) and potassium nitrate (30 wt%) with lesser concentrations of sodium sulfate, sodium chloride, and traces of other salts. While the nitrate compounds are strong oxidizers, particularly when heated, the only combustible compound in the mixture was EDTA (at 1 wt%), which provided only a trace of fuel for the nitrate oxidizers. Accordingly, heating this mixture was expected to result in only minimal exothermic reactions. As shown in Figure I-5, the heating rate for the nitrate salt drum contents was slightly faster than for the shakedown test and much slower than for the organic sludge test (Drum 1). For the nitrate salt test, heater power was applied for approximately 65 hours, at which time the temperature of the drum contents peaked at approximately 185°C (365°F). The off-gas was sampled and analyzed for the four VOC compounds of the organic sludge surrogate and for hydrogen chloride and chlorine gas. As expected, since the feed did not contain VOCs, VOCs were not detected in the off-gas. The feed material contained a relatively minor source of chlorine (3 wt% sodium chloride); however, hydrogen chloride and chlorine gas also was not detectable in the off-gas, most likely because the temperatures were not sufficient to decompose sodium chloride.

Posttest examination of the drum contents and heater assembly showed that the nitrate salt feed material had foamed, nearly plugging the test drum off-gas outlet and clearly indicating some degree of thermal decomposition of the drum contents. Figure I-9 shows a photograph of the contents of the drum after the heating process was completed and the drum had cooled. Laboratory analysis of pretest and posttest drum solids indicated that the nitrate concentration of the feed was essentially unchanged by processing, suggesting relatively minor decomposition or other removal of the nitrate salts. As shown in Table I-4, the feed material contained 1 wt% disodium hydrogen phosphate heptahydrate. Disodium hydrogen phosphate heptahydrate undergoes loss of five waters of hydration at 48.1°C (118.6°F). Therefore, the foaming may have been principally due to loss of water vapor from the disodium hydrogen phosphate heptahydrate.

The MSE concluded that during the nitrate salt test, the feed material partially melted and foamed. However, based on nitrate analysis of the pretest and posttest solids, there was little or no decomposition of the nitrate salts, which is consistent with the drum temperatures observed and the published decomposition temperatures for sodium nitrate and potassium nitrate (380°C [716°F] and 400°C [752°F], respectively). An additional conclusion, as expected from the pretest safety analysis, was that an oxidizing feed material, in the absence of an organic fuel, could be safely processed in the drum test system.



Figure I-9. Final drum contents from test of mixture of nitrate sludge surrogate.

#### **I-4.3 Organic Sludge with Combustible Debris Test (Drum 3)**

The objective of the organic sludge with combustible debris test was to simulate, at drum scale, ISTD treatment of a mixture of organic sludge surrogate, combustible debris surrogate, and water, while monitoring heating rates, apparent reactivity, and off-gas generation for the mixture.

The feed material, called organic combustible surrogate, was a mixture of organic sludge surrogate, a combustible debris surrogate, and water. The combustible debris surrogate was prepared from cotton rags (40 wt%), paper towels (40 wt%), polyethylene beads (10 wt%), ABS plastic beads (5 wt%), and PVC plastic beads (5 wt%). The overall organic sludge with combustible debris feed formulation was 35 wt% organic sludge, 55 wt% combustible debris, and 10 wt% water.

As shown in Figure I-5, the peak temperature for the organic sludge with combustible debris drum contents was 910°C (1,670°F), observed at 13.5 hours from the start of heating at the inner bottom thermocouple. Peak temperatures and times for the middle and outer thermocouples were 617°C (1,142.6°F) at 18 hours and 423°C (793.4°F) at 18.5 hours, respectively.

As shown in Figure I-5, both the rate of temperature rise and the peak temperatures were substantially greater than the tests for shakedown, organic sludge (Drum 1), or nitrate salt (Drum 2). Similarly to the organic sludge test, the rapid rise in temperature apparently was due to combustion of the drum contents. In this case, combustible materials included rags, paper, and plastic, as well as the oil and chlorinated solvents contained in the organic sludge feed. Although the organic sludge and combustible

debris feed included 10% water, the heat required to evaporate water apparently did not offset the additional thermal energy available from the combustible debris constituents and an increased airflow rate.

As noted above, off-gas from the test of Drum 1 organic sludge showed high concentrations of hydrogen chloride and the four VOCs included in the feed material, as indicated in Figure I-6. As discussed in that test, off-gas hydrogen chloride peaked at 33 vol% near the beginning of the test, and off-gas volatile organics peaked near 10 vol% later in the test. These off-gas components were derived from the halogenated solvent constituents of the organic sludge feedstock.

The Drum 3 organics with combustibles feedstock included the organic sludge surrogate (with halogenated solvents) at about one-third the concentration of the test of Drum 1 organic sludge. Consequently, the test of Drum 3 would be expected to show a pattern of off-gas hydrogen chloride and volatile organic generation similar to Drum 1. Drum 3 off-gas hydrogen chloride and volatile organics are shown in Figures I-10 and I-11, respectively.

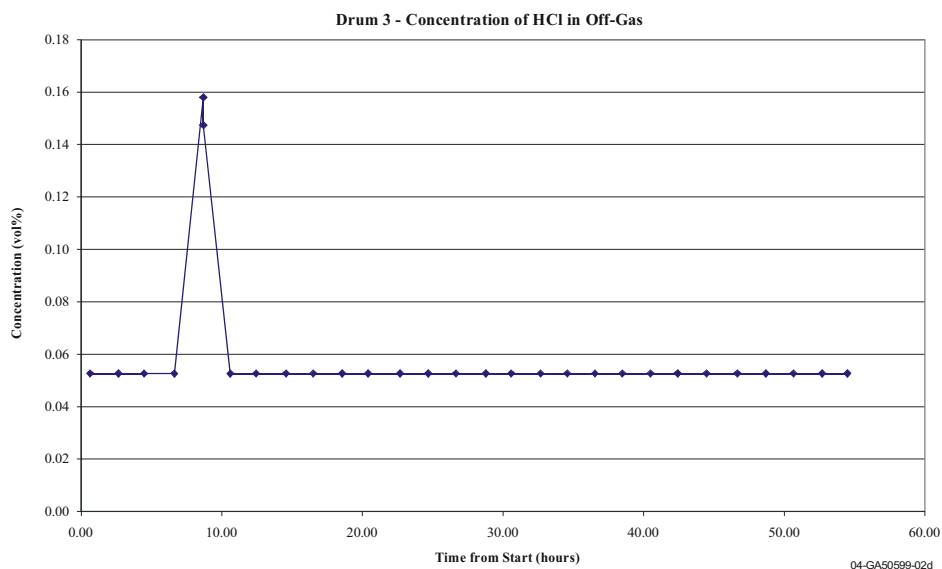


Figure I-10. Off-gas hydrochloric acid observed during the test of Drum 3 organic sludge and combustible debris.

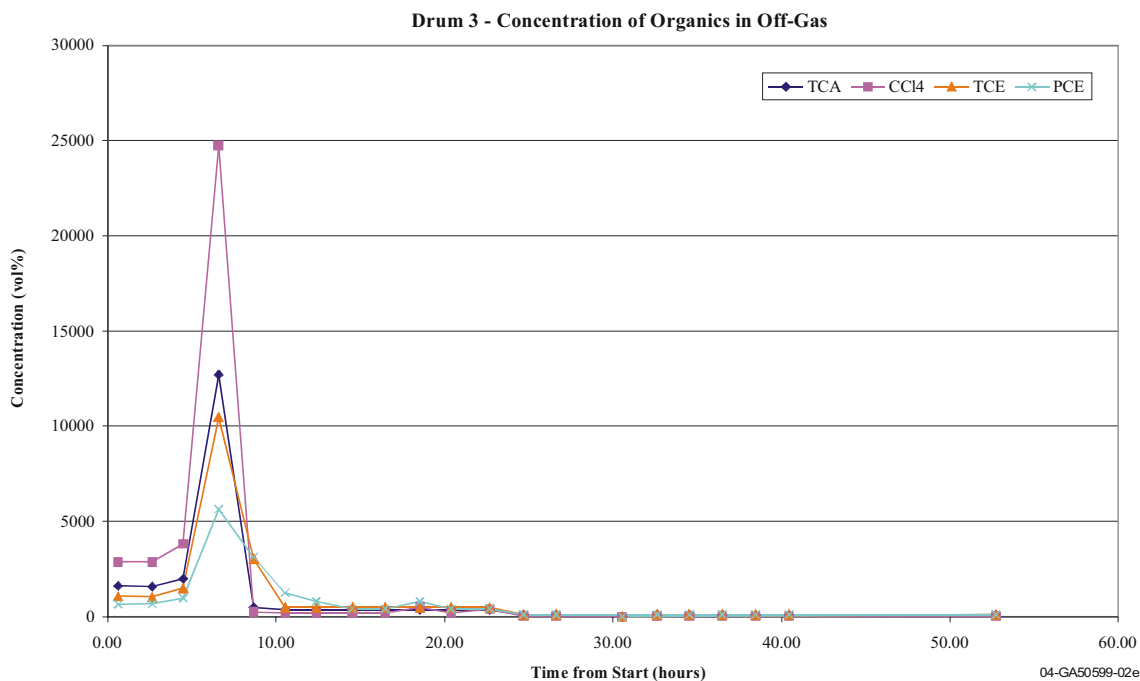


Figure I-11. Off-gas volatile organic solvents observed during the test of Drum 3 organic sludge and combustible debris.

Comparison of the Drum 3 results (Figures I-10 and I-11) to the Drum 1 results (Figure I-6) indicates much lower off-gas hydrogen chloride and volatile organic concentrations. The Drum 1 results were explained as combustion of halogenated solvents to hydrogen chloride (and carbon dioxide and water) during the early part of the test and volatilization, but poor combustion during the later part of the test. Following this reasoning, the Drum 3 off-gas should show either high concentrations of hydrogen chloride during good combustion or elevated concentrations of volatile organics during poor combustion. Since drum content temperatures were high during the Drum 3 test, the feed halogenated solvents must have volatilized, raising the question of what happened to the chlorine in the halogenated solvents. It appears to have neither burned to hydrogen chloride nor come off unaltered as volatile organics.

Analysis of posttest drum contents showed low concentrations of residual halogenated organic feed constituents, less than 150 mg/kg in all instances. Figure I-12 shows a photograph of the contents of the drum after the heating process was completed and the drum had cooled.



Figure I-12. Final drum contents from test of mixture of organic sludge and combustible debris surrogates.

Possible alternative fates of feed chlorine are that hydrogen chloride was scrubbed by feed constituents, which seems unlikely since there were no alkaline components in the Drum 3 feedstock, or that the halogenated solvents partially pyrolyzed, and the chlorine in the halogenated solvents came off as chlorinated organic combustion products. Rapid heating of the Drum 3 contents may have resulted in incomplete combustion, or the rapid heating and associated evident burning of combustible debris may have caused an off-gas dilution effect caused by rapid generation of large volumes of off-gas.

The test for Drum 4, discussed below, also included organic sludge surrogate as one component of its feedstock.

#### **I-4.4 Organic Sludge with Combustible Debris and Soil Test (Drum 4)**

The objective of the organic sludge with combustible debris and soil test was to simulate, at drum scale, ISTD treatment of organic sludge surrogate, combustible debris surrogate, and the soil surrogate, while monitoring heating rates, apparent reactivity, and off-gas generation for the mixture.

The feed material, called organics with combustibles and soil, was a mixture of the organic sludge (40 wt%), combustible debris (30 wt%), and soil containing a tracer (30 wt%), as shown in Table I-6. Also shown in the table, the tracer-containing soil consisted of 83 wt% soil from the INL Site, 15 wt% water, and 2 wt% ceric oxide. The other constituents (i.e., organic sludge and combustible debris) were shown in Table I-6 and were discussed previously for the formulas for Drum 1 and Drum 3 feeds. The soil mixture with tracer simulates the soil covering the waste buried at the SDA.

As shown in Figure I-5, the peak temperature for the drum contents was 619°C (1,146 °F), observed at 46.8 hours from the start of heating at the inner bottom thermocouple. Peak temperatures and

times for the middle and outer thermocouples were 344°C (686 °F) at 138 hours at the middle bottom thermocouple and 600°C (1,112 °F) at 144 hours at the outer bottom thermocouple. Note that the outer bottom thermocouple, and to a lesser extent the outer top thermocouple, showed a spike in temperature near the end of the test. During most of the test, the outer bottom thermocouple registered the lowest temperature of all the drum content thermocouples, as would be expected. However, for approximately 10 hours near the end of the test, the outer bottom thermocouple crossed over and registered the highest temperature in the drum during that period and nearly the highest temperature of any thermocouple for the entire test. Assuming that the high temperature reading was not a malfunction, which seems unlikely since the outer top thermocouple also registered a temperature rise during the same period, the only apparent cause of the temperature spike would have been delayed burnout of the drum contents near the outside of the drum.

As shown in Figure I-5, the peak temperatures for the Drum 4 test were greater than for the tests for shakedown, organic sludge (Drum 1), or nitrate salt (Drum 2) but less than the test of Drum 3 organic sludge with combustible debris. With the exception of the outer thermocouple temperature spike near the end of the test, the general rate of temperature rise for Drum 4 was less than that observed for all but the shakedown test.

Interestingly, the heating rate rank for each test corresponded to the fraction of fuel available in the feed material, as shown in Table I-7.

Table I-7. Rank of heating rates and fraction of fuel available in the test feed material.

Test	Fuel Fraction in Feed (sum of oil, solvents, and combustible debris) (wt%)	Rank for Heating Rates
Shakedown (soil and water)	0	5
Drum 1 (organics)	78	2
Drum 2 (nitrates)	1	4
Drum 3 (organics and combustible debris)	82	1
Drum 4 (organics, combustible debris, and soil)	61	3

Drum 4 off-gas hydrogen chloride and off-gas halogenated organics are shown in Figures I-13 and I-14. Comparison of results from Drum 1 (Figure I-6), Drum 3 (Figures I-10 and I-11), and Drum 4 shows a closely similar pattern of off-gas hydrogen chloride and halogenated organic evolution for Drum 3 and Drum 4 tests, with both differing substantially from Drum 1, which showed much higher concentrations of off-gas hydrogen chloride and off-gas halogenated organics. The peak hydrogen chloride and halogenated organic concentrations for Drum 4 occurred between 15 and 20 hours from the start of the test, while peak concentrations for Drum 3 were between 5 and 10 hours from the start of the test. This appears to be consistent with the slower heatup rate for Drum 4, which was expected because of the lower fuel content for Drum 4 feedstock.

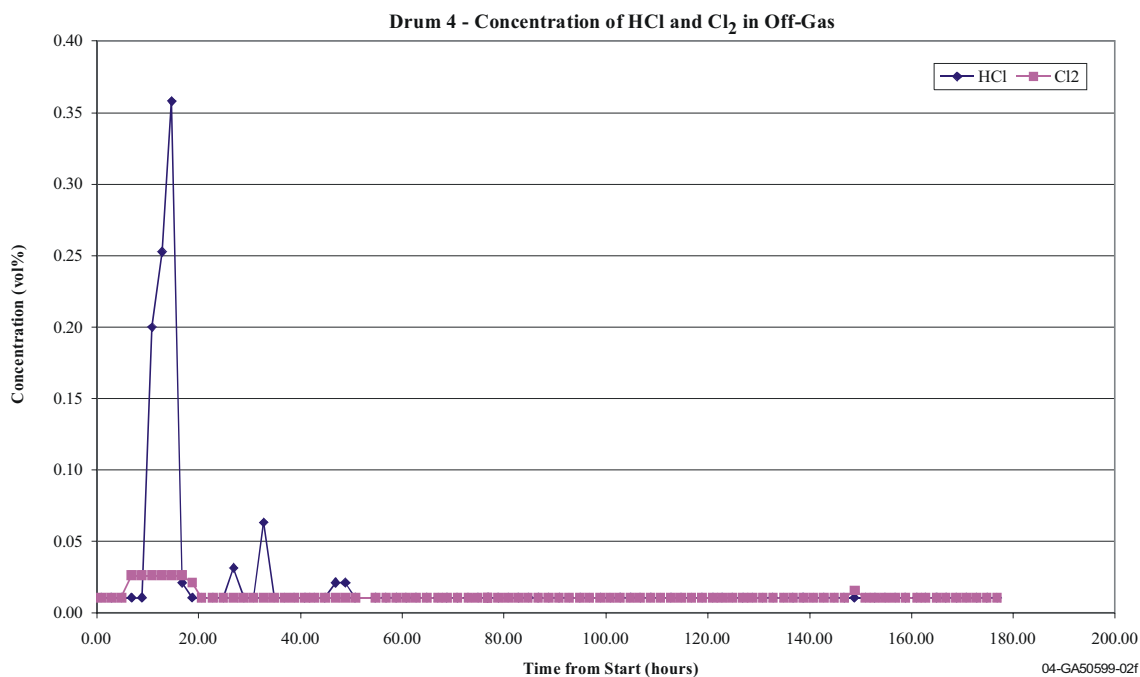


Figure I-13. Off-gas hydrochloric acid observed during the test of Drum 4 organic sludge with combustible debris and soil.

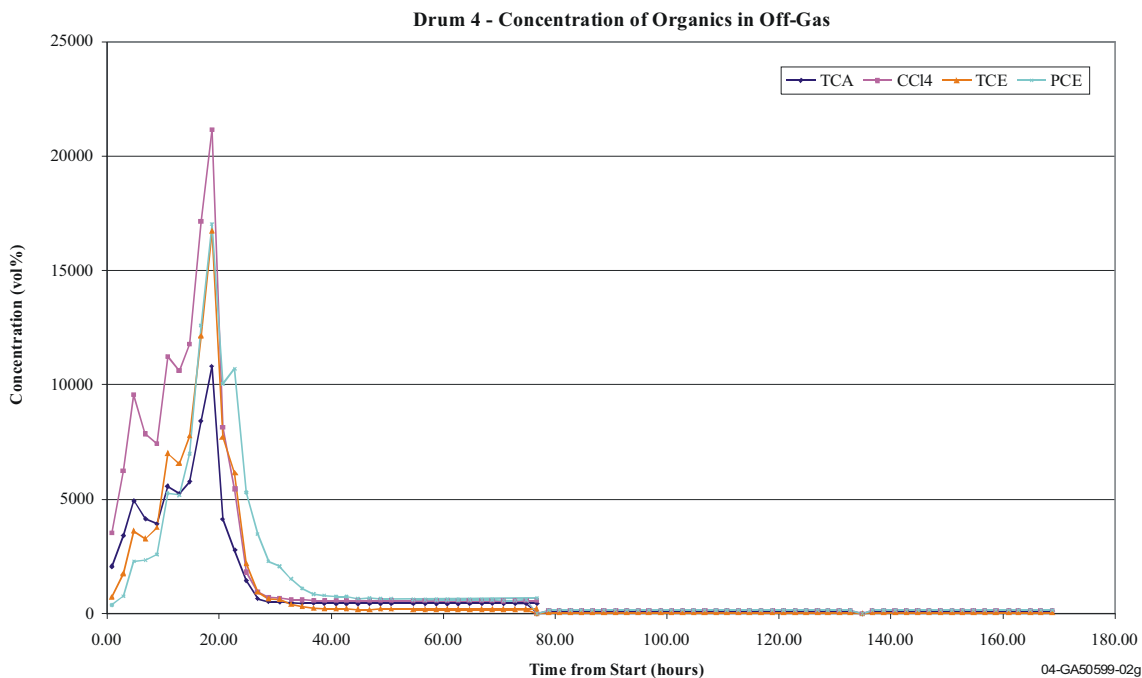


Figure I-14. Off-gas volatile organic solvents observed during the test of Drum 4 organic sludge with combustible debris and soil.

Posttest analysis of Drum 4 contents showed very low concentrations of residual halogenated organic feed constituents, generally undetectable, and less than 1 mg/kg in all instances. Figure I-15 shows a photograph of the contents of the drum after the heating process was completed and the drum had cooled.



Figure I-15. Final drum contents from test of mixture of organic sludge, combustible debris, and soil surrogates.

Paralleling the discussion of the Drum 3 test results above, the lower concentrations of off-gas hydrogen chloride and halogenated organics for Drum 4 relative to Drum 1 may have been caused by evolution of chlorinated organic pyrolysis products of the Drum 4 feed constituents. To assess this possibility, several off-gas samples from Drum 4 were analyzed using complete mass spectral scans of the sample gas chromatograms. Complete mass spectral scans can reveal and tentatively identify miscellaneous organic compounds in the analysis sample. In this case, analysis of Sample 10, which was taken 16.7 hours from the start of the test, showed relatively high concentrations of partial decomposition products, including benzene, styrene, and several chlorinated organic compounds. Generated over the entire test period, the Drum 4 chlorinated decomposition products might have accounted for the bulk of the chlorine present in the Drum 4 feedstock.

Chlorine balance aside, results from Drum 1, Drum 3, and Drum 4 show substantial concentrations in the off-gas of hydrogen chloride, feed halogenated organics, and partially decomposed feed organics. This suggests the need for an off-gas collection and treatment system during ISTD of halogenated organic-containing buried waste.

## I-5. RESULTS AND CONCLUSIONS

The MSE completed one drum-scale shakedown test and four drum-scale waste treatment tests. The waste treatment tests used surrogates for organic sludge; nitrate salts; a mixture of organic sludge and combustible debris; and a mixture of organic sludge, combustible debris, and soil containing a tracer. The organic sludge surrogate contained a mixture of cutting oil, halogenated solvents, and inorganic adsorbents. The nitrate salt surrogate consisted primarily of sodium and potassium nitrates. The combustible debris surrogate was a mixture of cotton rags, paper, and plastic beads. The soil containing a tracer was a mixture of soil from the INL Site, water, and ceric oxide. A mixture of water and soil, formulated to simulate the heat of vaporization of the organic sludge halogenated solvents, was used for the shakedown test. Heatup rates for the organic, nitrate, organic sludge with combustible debris, and organic sludge with combustible debris and soil feedstocks were compared to the heatup rate for the noncombustible shakedown feed. Faster heating rates were noted for the organic sludge, organic sludge with combustible debris, and organic sludge with combustible debris and soil feedstocks and were assumed to be due to combustion of halogenated solvents, oil, rags, paper, and other fuels in the various feedstocks.

The feedstocks containing significant quantities of combustible materials were essentially self-heating after an initial heatup period, provided that combustion air was supplied to the test drum. The self-heating of combustible drum contents appeared to produce gaseous partial-decomposition products, though supplying electrical power to the heater assembly appeared to be necessary for more complete combustion of the gaseous partial-decomposition products. However, the bulk of the heating power for the drum contents came from combustion of drum contents. The rate of heatup of the drum contents corresponded to the relative amount of fuel in the feedstocks. For these tests, the rate of heating increased in the following order: shakedown (soil and water), Drum 2 (nitrate sludge surrogate), Drum 4 (organic sludge, combustible debris, and soil), Drum 1 (organic sludge), and Drum 3 (organic sludge and combustible debris).

Drum 1 (organic sludge), Drum 3 (organic sludge with combustible debris), and Drum 4 (organic sludge with combustible debris and soil) tests used feedstock containing halogenated solvents. In the Drum 1 test, the off-gas initially contained high concentrations of hydrogen chloride and later relatively high concentrations of feedstock halogenated organics. This was attributed to initial complete combustion of halogenated organics to hydrogen chloride, carbon dioxide, and water, followed by a period of obvious noncombustion of volatilized halogenated organics. The noncombustion of halogenated organics was apparently caused by removing electrical power from the heater assembly and discontinuing combustion air to the drum, which was done in order to stop the test.

Compared to the Drum 1 test, off-gas from the Drum 3 and Drum 4 tests showed lower concentrations of both hydrogen chloride and feed volatile organics. Semiquantitative organic scans of selected off-gas samples suggested that for Drum 3 and Drum 4, much of the feed halogenated organics may have been converted to chlorinated partial decomposition products. In any case, off-gases of those seen for Drum 1, Drum 3, and Drum 4 would ordinarily require additional treatment before discharge to the atmosphere.

As expected, organics were not detectable in off-gas from the Drum 2 nitrate salt test.

The MSE concluded that the heater assembly performed as expected, gradually heating surrogates of buried organic sludge, nitrate salts, organic sludge with combustible debris, and organic sludge with combustible debris and soil. Heating feedstocks containing halogenated organics resulted in emission of hydrogen chloride, chlorinated decomposition products, and unaltered feed organics, indicating a need for downstream off-gas treatment of buried waste containing high concentrations of organic constituents.

A secondary conclusion was that organic sludge alone, nitrate salts alone, and organic sludge with combustible debris could be tested safely in the drum-scale test bed. However, drum scale tests conducted at the Energetic Materials Research and Testing Center (discussed in Appendix J) showed that there were conditions where uncontrolled exothermic reaction could occur. Mixtures of organic sludge or combustible debris with nitrate salts, a combination of fuel and oxidizer, were not tested. Fuel with oxidizer mixtures of this type was tested at the Energetic Materials Research and Testing Center in New Mexico. The results of those tests are reported separately.



## **Appendix J**

### **ISTD Reactivity: Energetics Materials Research and Testing Center**



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## Appendix J

### ISTD Reactivity: Energetics Materials Research and Testing Center

The reactivity studies for in situ thermal desorption (ISTD) were conducted in two laboratories and are presented in two parts:

- Appendix H—results of tests conducted at the Idaho National Laboratory Site using differential scanning calorimetry on nonradioactive isotopes
- Appendix J—results of tests conducted at the Energetic Materials Research and Testing Center (EMRTC) on drum-scale nitrate salt reactivity, where mixtures would undergo chemical reactions leading to innocuous products without explosions or runaway reactions.

The objective of nitrate salt reactivity testing was to determine temperature regimes where mixtures would undergo chemical reactions leading to innocuous products without explosions or runaway reactions. Nitrate salts simulating Series 745 sludge from Rocky Flats Plant (RFP) were heated with several other surrogates at drum scale under conditions similar to ISTD. The surrogate included graphite powder, cutting oil mixed with chlorinated degreaser solvents, and mixed paper and plastic combustibles. In each test, control of the reaction was lost, leading to vigorous ejection of reactants and products from the drum and to destruction of portions of the apparatus.

These tests were carried out at EMRTC at New Mexico Institute of Mining and Technology.

#### J-1. IN SITU THERMAL DESORPTION OVERVIEW

Data from reactivity tests will be used to help evaluate the potential of ISTD as a viable treatment option for debris-type waste buried in the Subsurface Disposal Area (SDA). Tests were performed at both laboratory scale and drum scale. Laboratory-scale tests were used to evaluate results using small quantities of waste and are described in Appendix H. The drum-scale tests more closely simulated the thermal, mass, and time parameters that would exist in the field. This testing was done to demonstrate effectiveness and to verify implementability as defined below:

- Effectiveness—determine the degree of hazardous organic contaminant and nitrate removal or destruction from waste
- Implementability—test potential mixtures of organics and nitrates for reactivity.

Results are described below of slowly heating graphite, combustible debris, organic sludge, and nitrate salt sludge, simulating the ISTD process. An ISTD central well was used to heat drum-scale waste material of simulated nitrate salts, mixed waste with graphite, debris (paper or plastic), and organic sludge (machine cutting oils).

The ISTD process is designed to destroy or remove organic material underground, particularly chlorinated solvents. All previous remediation using ISTD has been of contaminated soil sites (Vinegar, Stegemeier, and Sheldon 1997). However, using ISTD at the Radioactive Waste Management Complex would heat not only drums of waste including targeted solvents, but also drums containing

nitrate salts. During waste heating, these nitrate salts could melt and become potential oxidizers. There is no field information on reactivity when slowly heating collocated drums of organic sludge (RFP Series 743 and 744) and nitrate salts (RFP Series 745).

Selected mixtures of simulated waste using both laboratory and field methods were tested for reactivity. Larger-scale bench and field reactivity testing was performed to support thermal in situ treatment and retrieval safety assessment (Dick 2001; Dick 2003); this testing used external band heaters on simulated organic sludge, graphite, or debris with nitrate salt mixtures. Mixtures were heated in 5- and 55-gal drums while temperature was monitored. The heating rate and temperature gradient within the waste were much higher than would be experienced under ISTD conditions. Specific reactive tests were run at the bench scale on surrogate mixtures.

Reactivity testing slowly heats the combined oxidizer (nitrate salts) and waste streams containing carbon. Recent retrieval of waste by the Glovebox Excavator Method Project<sup>a</sup> indicates that though drums are generally corroded, the plastic bags containing the waste within the drum are still frequently intact and surrounded by soil. Slowly heating this waste material will remove soil moisture, melt nitrates, and vaporize or char organic material. Molten salts that flow may first go through surrounding soil before encountering organic material. Though the overall percentage of salts in the waste is small, suggesting a limited contact area, the surrogate was combined, mixed, and tested to simulate bounding conditions for reactivity between nitrate salts and organic compounds.

Section 4.2.4 of Yancey et al. (2003) describes the reactivity testing. The following section reports results of heating that simulate (at drum scale) ISTD of mixtures of nitrate salts containing organic sludge surrogate and graphite. This augments the laboratory measurements using nitrate salt mixed with organic sludge surrogate and debris surrogate described in Appendix H.

## **J-2. SUMMARY OF DRUM-SCALE REACTIVITY TEST**

The purpose of this test series was to slowly heat carbon containing RFP waste surrogates with nitrate salt surrogate so as to destroy most organics without causing excessive reactivity. Reactivity was found to be a function of heating rate, physical arrangement of surrogates, and containment of the molten salts for an extended period of time. Each test exhibited some combustion reactions by pressure venting, burning, or building up pressure and blowing the lid from the drum. There were no detonations.

Three waste surrogates containing carbon were tested: (1) graphite powder, (2) organic sludge, and (3) combustible debris. Four heating campaigns were conducted, two being run on the first mixture of graphite powder and nitrate salts.

Test 1 was performed on a full drum of graphite powder thoroughly mixed with nitrate salt surrogate. The first heating (Phase 1) involved slow cycling the central heater and additional heat added from the outside using low-wattage, home roof gutter heaters around the drum, which was not insulated. Cold weather caused a maximum center temperature of only 250°C (482°F) and a drum wall temperature of 125°C (257°F) to be achieved over a period of 15 days.

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a. The Operable Unit 7-10 Glovebox Excavator Method Project retrieved 59 m<sup>3</sup> (77 yd<sup>3</sup>) of buried waste from the SDA during December 2003 and January 2004 (DOE-ID 2004). The purpose of the Glovebox Excavator Method Project was to demonstrate the feasibility of waste retrieval, provide information on any contaminants of concern present in the underburden, and characterize waste-zone material for safe and compliant storage pending a decision on final disposition. The Glovebox Excavator Method Project operated under the *Federal Facility Agreement and Consent Order for the Idaho National Engineering Laboratory* (DOE-ID 1991) and the "Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA/Superfund)" (42 USC § 9601 et seq., 1980).

After the drum cooled, insulation was added around the gutter heaters for the second heating campaign. Phase 2 of Test 1 also lasted for about 15 days. The added insulation allowed the entire mixture to achieve a higher temperature, resulting in more consistent temperatures between the drum wall and the center. As the temperature of the system rose, the heater was programmed for an increasing heating rate, which caused it to cycle faster. During the final stages of the test, the heat controller was removed, and the heater remained on continuously. A reaction occurred at a center temperature slightly above 425°C (797°F), reaching 535°C (995°F) and a radius temperature of 445°C (833°F) before instrumentation was lost. The resulting reaction caused an elevated pressure ejection of the molten test mixture.

Test 2 was performed on a large amount of organic sludge surrogate containing chlorinated solvents and Texaco Regal oil absorbed on Microcel E, a commercial-grade calcium silicate. Heating was controlled by cycling the heater on and off. The test was the shortest of the series, lasting about 3 days. The chlorinated solvents evaporated rapidly while the oil reacted with both air and nitrate salts and evaporated. Eventually, oil collected in the insulation and subsequently ignited and burned. The burn destroyed the thermocouple wires, causing extensive “noise” in the test data output. The data collected are quite difficult to interpret, but the best estimate is that the burning or nitrate reaction occurred at approximately 250°C (482°F). Almost all the organic sludge surrogate apparently reacted or evaporated leaving a residue of gray or white material that was 25 cm (10 in.) thick and covered the entire diameter of the drum. The residue adhered to the drum and was difficult to remove but was highly water soluble.

Gas sampling equipment took periodic samples of the off-gases of this test of organic sludge with nitrate salts. Off-gas condensate, chlorinated solvents, and oil also were evolved in Test 2. Weight loss was measured during the test but could not be determined after reactions disrupted the system.

Test 3 was performed on combustible debris mixed with nitrate salts. Heating was controlled by cycling the heater 100°C (212°F) above the center test mixture temperature. After 5 days of heating, the debris reacted or burned, and the resulting pressure blew the lid from the drum. Thermocouples recorded a reaction temperature of 220°C (428°F). Since the drum was very large compared to the small volume sampled by just three thermocouples, reaction temperature has a certain degree of uncertainty; the reaction may have started in an area away from temperature probes. Salts also melt around this temperature at 212°C (413.6°F).

Test 3 reacted at the lowest temperature. Ignition temperature of cellulose or its reactivity with molten salts was lower than decomposition temperature of the surrogate salts. Test 2, though short, generated the most data, weight loss, off-gas, off-gas condensate, and solid residue. Collection and ignition of oil in insulation were not expected. Apparently, oil-laden gases vented out the air intake tubes. Phase 1 of Test 1 successfully showed that long-term heating of a reactive mixture could be maintained with a normal temperature gradient. The second heating increased the temperature gradient in the drum, resulting in a reaction and venting of the molten test mixture.

### **J-3. TEST OBJECTIVES, RATIONALE, AND DEVIATIONS FROM TEST PLAN**

Section 2.6.7 of Yancey et al. (2003) lists objectives for reactivity testing. The data from these tests support U.S. Department of Energy Idaho Operations Office implementability objectives (DOE-ID 1998) by determining whether subsurface heating of mixtures of organic and nitrate waste at operational temperatures and rate of increase can be done safely without having uncontrollable exothermic reactions.

The following reactivity tests were performed to determine whether uncontrolled reactions occur when heating some SDA waste:

- Laboratory measurements using thermal gravimetric analysis (TGA), similar to the proposed differential scanning calorimetry analysis with added weight-loss capability (described in Appendix H)
- Drum-scale, 55-gal reactivity tests using a full-scale ISTD vacuum-heater-well arrangement (described in this appendix).

Differences between laboratory and drum-scale experimental testing, besides the difference in scale, include:

- Type of heating
- Heating rate
- Waste material temperature gradient
- Waste material mixes
- Physical arrangement of salts and organics
- Gas removal.

The objective of the drum-scale testing was to determine the occurrence of exothermic reactions between nitrate salt surrogate (surrogate for RFP Series 745 waste) and organic sludge surrogate (surrogate for RFP Series 743 waste), graphite, or debris that might be encountered during ISTD remediation of buried waste. Drum-scale tests were performed by slowly heating—in a way similar to ISTD—mixtures of nitrate salts and carbon-containing surrogates of graphite, organic sludge, and debris. Data obtained include weights, temperatures, off-gas and residue samples, and qualitative observations of reactions.

Current thermal testing simulates conditions more like ISTD that were not found in previous drum-scale testing (Dick 2001; Dick 2003):

- Heating rate is slower to allow for the induction period that might occur at slower rate
- Heating method is internal with vapor removal from center through the heater
- Heat progressively moves out from a center point, giving a large temperature gradient from heat source and limiting the mass at any one temperature
- As heating progresses, mass and off-gas data are recorded to help interpret qualitative observations.

The past test heating rate of 400°C (720°F)/day (0.3°C [0.54°F]/minute) and even current rate of 0.1°C (0.18°F)/minute is still faster than ISTD would be for any substantial quantity of material in the field. In these large-scale reactivity tests, drum center temperature was usually ramped from 25 to 200°C (77 to 392°F) in the first day by cycling the heater on and off.

## J-4. EXPERIMENTAL DESIGN AND PROCEDURES

The basic experimental sequence for drum-scale reactivity testing is shown below:

1. Prepare surrogates for waste and contaminants
2. Place samples in heating container (drum), connect thermocouples and off-gas system, and place on balance
3. Slowly heat drum while recording temperatures, weight loss, off-gas, and qualitative behavior
4. After target temperature is reached, cool and sample.

### J-4.1 Drum-Test Setup

Each experiment was performed in a 55-gal drum with a removable lid and ring. Stainless steel drums were used in the first two test mixtures in case some corrosion occurred during the test. Little corrosion was observed, so Test 3 was run in the available mild steel drum.

This test used a section of a full-scale, field-use TerraTherm heater well assembly for ISTD. The heating mechanism consisted of a 8-cm (3-in.) heating tube containing a 0.9 m (3-ft) nichrome heater rated at 800–1,000 W, 300 W/ft when run at 120 Vac (see Figure J-1). The voltage at the test site was between 121 and 122.2 Vac.



Figure J-1. ISTD ceramic, mounted nichrome wire.

The heating tube was fitted into a 10-cm (4-in.), stainless steel, slotted well casing (see Figure J-2). This was mounted on a flange and put into 55-gal drums with an internal diameter of 22.5 × 34 in. high. Stainless steel drums were used for both phases of Tests 1 and 2. When corrosion was determined not to be a significant problem, a cold-steel drum was used for Test 3. All hardware was stainless steel. The well casing reached to within a few inches of the bottom of the drum. The top of the well casing was attached to a tee of the same diameter, which allowed gas to be extracted from the side, and a top lid that locked the heater into place. An air inlet tube was installed to within 15 cm (6 in.) of the bottom of the drum near

the wall and 23 cm (9 in.) from the center. Six layers of high-density insulation were used between the bottom of the drum and the scale surface.

Four ungrounded thermocouples (0.6-cm [1/4-in.] diameter) were used in the drum to measure temperatures. The first thermocouple was installed in the heating tube with the heater. The second was located in the center of the sludge (as close as possible to the well casing). The third was located on the midradius. The fourth was located close to the inside wall (radius) of the drum.

The heating rate and other data were collected with an IOtech analog board mounted in a PC. Data were recorded in 15-second intervals. A camera was installed to view the computer screen, which allowed the temperature reading to be checked from an offsite location throughout the day and on weekends.

Two 36.6-m (120-ft) gutter heaters were wrapped on the outside of the drum to help maintain a higher ambient temperature than was otherwise possible during the winter months. These heaters were controlled with a separate thermocouple. They were only used for Phase 1 of Test 1 without insulation. In Phase 2 of Test 1 and all subsequent tests, four layers of high-density insulation were used around the drum.

An electronic scale with a capacity of 453.6 kg (1,000 lb) and a 0.23-kg (0.5-lb) readout measured the mass loss as the mixture was heated. The scale was provided with an extra long cable, which allowed the readout screen (data collected manually twice a day) and power supply to be located in the bunker.

After the first heating campaign in Phase 1 of Test 1, four layers of insulation were wrapped on the outside of the drum as well as on the top. Three of the layers were foil-backed for extra heat retention. In Phase 1, the weather enclosure was constructed of 2 × 4-in. studs and enclosed with black plastic. The enclosure proved to be unsatisfactory during the cold winter weather that continued throughout Phase 1. Plywood was added to the walls for Phase 2. Black plastic covered the top because wires from the AC heater and thermocouple as well as vent and vacuum lines leading from the drum made a fitted removable top very difficult to construct.

Gas was removed from the drum using a vacuum pump. During the test period the vacuum pump remained in continuous operation, pumping at a rate of 0.5 +/- 0.25 cfm. For Test 2 and part of Test 3, this gas was analyzed with a Testo furnace gas analyzer. The removal rate was increased for Tests 2 and 3 to 0.7 cfm using a second pump. For a portion of the first campaign of heating in Test 1, the vacuum pump was shut down to allow a higher temperature to be reached in the drum.



Figure J-2. ISTD 4-inch slotted, stainless steel pipe.

## J-4.2 Heating Strategy

The heating strategy for each test was generally the same: rapid heating until some minimum threshold temperature (100–200°C [212–392°F]) was reached, then a slow heating rate after these initial temperatures were achieved in the center of the drum. Details varied based on nature of the waste and response of the system. Heating rate and other data were collected with an IOtech analog board mounted in a personal computer. Thermocouple data were recorded in 15-second intervals.

Heating rates are shown in Tables J-1 through J-4. The rate was targeted to achieve a wall temperature of 450°C (842°F) at a heating rate of about 0.1°C (0.18°F)/minute. The typical field rate of 0.005–0.01°C (0.009–0.018°F)/minute is much slower than any of the testing. The heating rates from the heater alone ranged from the slowest in Phase 1 of Test 1—250°C (450°F)/6 days or 0.02°C (0.036°F)/minute for the center, and 125°C (225°F)/6 days or 0.01°C (0.018°F)/minute for the wall—to the fastest in Test 2—275°C (495°F)/2.5 days or 0.08°C (0.144°F)/minute for the center, and 225°C (405°F)/3 days or 0.05°C (0.09°F)/minute for the wall. These rates increased during combustion reactions.

Table J-1. Set points for temperature control for Phase 1 of Test 1.

Time (hours)	Heater Start Temperature (°C)	Heater Set Temperature (°C)	Interval Rate of Temperature Increase (°C/hour)	Average Rate of Temperature Increase (°C/hour)
1	0	200	200	200
4	200	200	—	50
5	200	400	200	80
6	400	425	25	71
10	425	400	—	40
11	400	200	—	18
12	200	400	200	33
14	400	200	—	14
16	200	400	100	25
18	400	400	—	22

Table J-2. Set points for temperature control for Phase 2 of Test 1.

Day	Time (hours)	Heater Start Temperature (°C)	Heater Set Temperature (°C)	Interval Rate of Temperature Increase (°C/hour)	Average Rate of Temperature Increase (°C/hour)
1	24	0	250	10.4	10.4
3	72	250	300	1.0	4.2
5	120	300	300	—	2.5
6	144	300	325	1.0	2.3
7	168	325	325	—	1.9
8	192	325	350	1.0	1.8

Table J-2. (continued).

Day	Time (hours)	Heater Start Temperature (°C)	Heater Set Temperature (°C)	Interval Rate of Temperature Increase (°C/hour)	Average Rate of Temperature Increase (°C/hour)
8.6	206	350	375	1.7	1.8
11.9	286	375	375	—	1.3
12.3	295	375	400	2.6	1.4
13.8	331	400	400	—	1.2
14.2	341	400	425	2.6	1.2
14.9	358	425	425	—	1.2
15.1	362	425	530	21.9	1.5

Table J-3. Heater set points for temperature control of Test 2: organic sludge and nitrate salts.

Day	Time (hours)	Heater Start Temperature (°C)	Heater Set Temperature (°C)	Interval Rate of Temperature Increase (°C/hour)	Average Rate of Temperature Increase (°C/hour)
1	24	0	200	8.3	8.3
2	48	200	225	1.0	4.7
3	72	225	250	1.0	3.5
6	144	300	325	1.0	2.3
7	168	325	325	0.0	1.9

Table J-4. Heater set points for temperature control of Test 3: debris and nitrate salt.

Time (hours)	Heater Start Temperature (°C)	Heater Set Temperature (°C)	Interval Rate of Temperature Increase (°C/hour)
0	25	0	0
10	220	37.0	37
20	210	2.0	20
50	250	1.0	10
110	300	0.8	4.6
120	300	0.8	3.3
130	320	0.8	2.7

#### J-4.2.1 Test 1 Graphite Heating Rate

Phase 1—Heating rate (ramp rate) for the mixture was set at 1°C (33.8°F)/hour. The experiment was interrupted several times for adjustments, but heating was maintained at a constant rate, restarting at the temperature of interruption.

Phase 2—Heating rate (ramp rate) for the mixture was set to reach 200°C (392°F) the first day. The experiment was not interrupted until the reaction, but several hold points at constant temperature

occurred. The heater continued to cycle regularly with a cycle time of approximately 1 hour until it was removed from the controller and plugged directly into the wall electric outlet. Heating rate was initially 1°C (33.8°F)/hour, but it was increased to 1.7°C (35.06°F)/hour and then to 2.6°C (36.68°F)/hour between hold points.

#### **J-4.2.2 Test 2 Organic Sludge Heating Rate**

The heating strategy for Test 2 was to heat the sample at 5°C (41°F)/hour until the drum reached a temperature of 200°C (392°F). Once the temperature reached 200°C (392°F) at the center thermocouple, the heating rate was reset to 1°C (33.8°F)/hour.

#### **J-4.2.3 Test 3 Combustible Debris Heating Rate**

The heating strategy for Test 3 was to heat the sample rapidly at 10°C (50°F)/hour until the drum reached a temperature of 100°C (212°F). Once the temperature reached 100°C (212°F) at the center thermocouple, heating rate was reset to 1°C (33.8°F)/hour. The heater was allowed to cycle only 100°C (212°F) above the set point of the sample center temperature throughout the test.

### **J-4.3 Gas Removal and Sampling**

Gas was removed from the drum using a vacuum pump. During Test 2 and part of Test 3, this gas was analyzed with a semicontinuous sampling monitor. For Test 1, the removal rate was 0.6 cfm but decreased to 0.5 cfm after 2 days. During Tests 2 and 3, the removal rate was higher: 0.8 cfm with the use of two pumps. Test 2 also had condensate samples removed each day of the test. Two large Cuno water-type filter holders without the filters were used as knockout containers to adequately handle the large volume of condensate produced. The vacuum pump was shut down temporarily in Test 1 to assist in achieving a higher temperature inside the drum.

### **J-4.4 Surrogate Mixtures**

The three carbon-containing surrogates were chosen because they simulate prevalent carbon-containing waste types that might be encountered in RFP waste and are similar to those used in previous small- and large-scale tests for data comparability.

There is some graphite in the waste from graphite molds, and reactivity of this material has been extensively studied (Dick 2003). Graphite, however, is a small portion (0.2%) of the waste and carbon-containing material in the SDA. Debris used here is combustible trash, primarily plastic and paper. The combustibles, when heated, will char, forming some form of carbon. They comprise up to 40% of the waste volume. Organic sludge surrogate was prepared according to the best estimate of what was prepared at RFP and disposed of at the SDA (see Table A-3 of Appendix A). It has been used for grouting and already has been reactivity tested both by thermo analysis and in macrotesting. It contains four chlorinated solvents dissolved in machine oil and absorbed on a silicate media.

These three carbon-containing surrogates provide the full range of carbon-containing test materials covering the probable waste both physically and chemically in terms of reactivity that might be close to nitrate salts. In all these cases, however, intimate mixing at the scale, tested in a single intact drum, is probably not duplicated by any process in producing or in disposing of buried waste. Thus, all results are truly bounding and “worst case.” Excavations from Pit 9 indicate that drums have undergone extensive corrosion and decomposition, but waste packages are still discrete with bags intact. No intermixed separated containers were observed.

The surrogate mixtures were prepared according to the recipes in Appendix A. The nitrate salts were used in all tests and organic sludge formulation used for Test 2. Each drum was filled to within 5 cm (2 in.) of the top with the heater assembly in place. Actual weights of each mixture placed in the drum are in Table J-5. The following mixture weights were unavailable and estimated indirectly from previous tests and bulk densities:

- Test 1 was planned to be a mixture of 80% nitrate salt mix and 20% carbon in the form of powdered graphite
- Test 2 was planned to be 75% nitrate salt mix and 25% organic sludge containing Texaco Regal Oil and chlorinated solvents
- Test 3 was planned to be 75% nitrate salt mix and 25% combustible debris mix, consisting of paper and plastic.

Table J-5. Summary of drum-scale testing of nitrate salts and surrogates.

Carbon-Source Waste Surrogate Mixed with Salt Surrogate Mixture (60% sodium nitrate, 30% potassium nitrate, and 10% soluble salts)	Carbon- Containing Waste Surrogate (wt%)	Carbon- Containing Waste Surrogate (lb)	Nitrate Salts (lb)	Gross Weight (lb)	Tare Weight (lb) <sup>a</sup>	Weight Loss (lb)	Weight Loss (wt%)
Graphite powder (80 mesh)	20	71	282	531	178 <sup>a</sup>	3	1
Graphite powder (80 mesh)	20	70	280	528	178 <sup>a</sup>	46	13
Organic sludge, chlorinated solvents, oil, and solid absorbent	24.4	113	352	636	191 <sup>b</sup>	65	14
Debris—paper and plastic	14.2	26.5	160	378	191 <sup>b</sup>	<2	<1

a. Tare weight for Test 1 includes 55-gal stainless steel drum, lid, flange, “tee,” heater assembly, gutter heater top and bottom insulation, and associated 1-in. stainless steel tubing

b. Tare weight for Tests 2 and 3 includes 55-gal drum; lid; flange; “tee”; heater assembly; top, bottom, and side insulation; cement board; 5-gal stainless steel knockout pail; and associated 1-in. stainless steel tubing.

## J-4.5 Drum-Scale Equipment for ISTD Reactivity Testing

The offsite drum-scale testing included the following equipment:

- Reaction vessel 55-gal drum
- 10-cm (4-in.) slotted casing pipe
- Nichrome 150-W/ft heater elements in a stainless steel 6-cm (2.5-in.) heater can
- Off-gas analyzer
- Analytical instrumentation for solid assay of residues
- Vacuum vapor removal pump(s)
- Gas spargers and condensate knockout filters
- Thermocouples and data logger
- Flow meters

- Vacuum gauge
- Valves and associated piping
- 453.6-kg (1,000-lb) drum balance.

## **J-5. DATA MANAGEMENT, ANALYSIS, AND INTERPRETATION**

Except as discussed previously, data were recorded manually in log books. Each set of conditions was tested once; replicates were beyond the scope of this work.

## **J-6. RESULTS AND CONCLUSIONS**

The generic reaction between sodium nitrate and pure carbon proceeds according to equations such as Equation (J-1):



Nitrate organic reaction ratios vary, but the stoichiometric nitrate-to-carbon ratio of 85-to-15 can yield complete reduction to nitrogen gas and carbon dioxide and, thus, is the most exothermic of the reactions.

The organic portion of organic sludge is not pure carbon like charred debris, charcoal, carbon black, or graphite, but contains a paraffinic oil, which is 86% carbon. Debris before charring (cellulose) is 48% carbon. The decomposition of nitrate salts is endothermic like salt melting and requires a continual input of heat. Pyrolysis is also endothermic. Combustion occurred in all the tests because the vapor removal system drew air continually through the drum.

The experimental results are plotted as time and temperature curves. Mixtures of carbon and nitrate salts will react when heated through the very slow rate of a typical ISTD application in contaminated soil and debris applications. Reactions or decomposition occur above the melting point of the salt (212°C [413.6°F]) but below the target temperature of 450°C (842°F).

### **J-6.1 Graphite Phase 1**

There was some reaction and/or decomposition during the 15-day test run. The sample mass decreased by 1.4 kg (3 lb). There was a small accumulation of a deep reddish brown material collected in the air tube leading from the drum to the vacuum pump. The center of the drum may have approached optimum decomposition temperature, but the remainder of the drum could not be heated to a temperature sufficient to start decomposition. It was impossible to heat the outside of the drum above 120°C (248°F). Whether this was because of the capacity of the gutter heaters or an undiscovered (and undocumented) internal thermostat is not known.

The temperature profile of the test is found in Figures J-3 and J-4. Figure J-3 shows the heating profile. The heater made large high-to-low swings during heating since the center sample thermocouple, which was not immediately next to the heater, was used as the controller. Figure J-4 is a profile of the complete test. The temperature inside the drum cooled a little during the last part of the test. This cooling effect was attributed to a winter storm and cold weather that reduced the ambient temperature approximately 20 to 30°C (68 to 86°F).

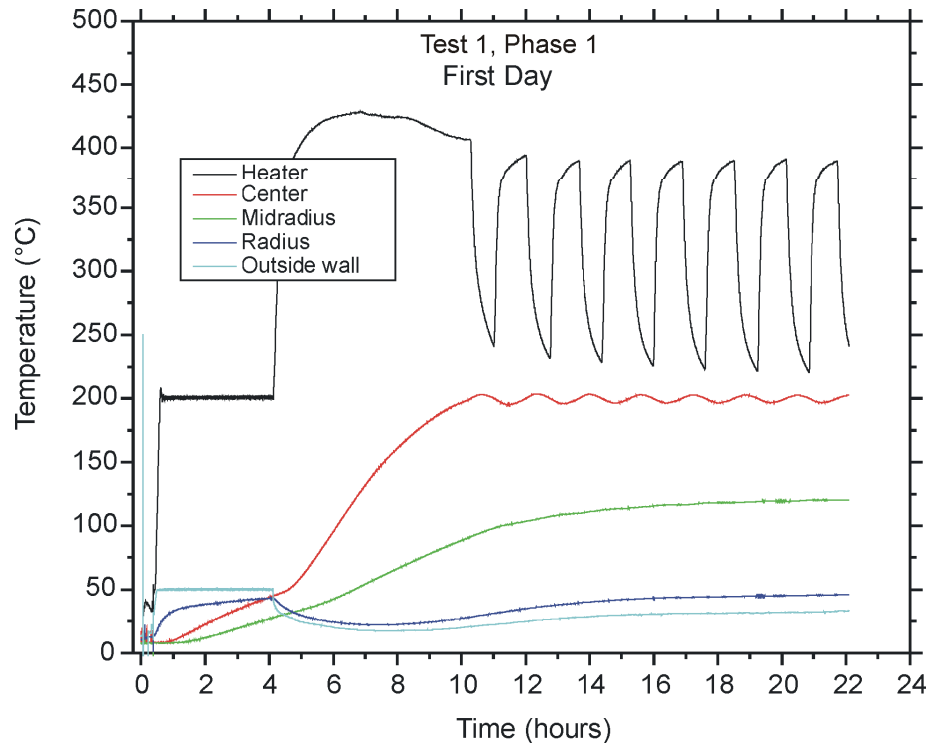


Figure J-3. Heating profile for the first day.

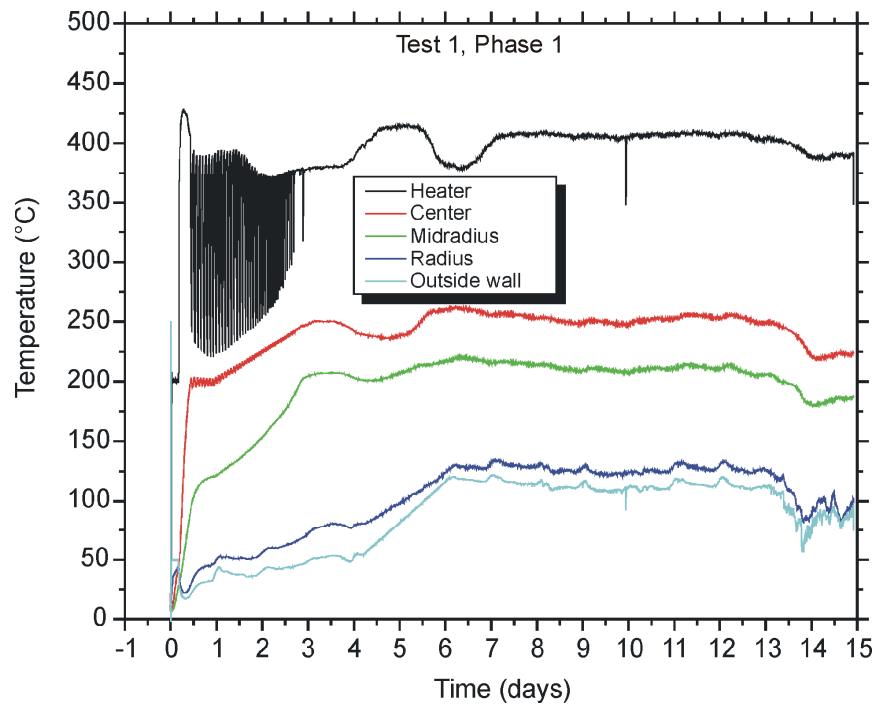


Figure J-4. Heating profile for duration of test.

## **J-6.2 Graphite Phase 2**

### **J-6.2.1 Physical Evaluation**

The test was terminated on the 15th day when a reaction reached a temperature and pressure high enough to bulge the lid, which caused seal failure on the right-hand side of the drum. This failure was followed by ejection of molten contents, which covered an area of soil and rocks for approximately 7.6 m (25 ft) outward. When hardened, the area had a silvery, shiny texture. There were several very large chunks of a soft coallike material in the sand beside the scale. Posttest, the interior of the drum contained about 6.67 cm (2.625 in.) of material. The surface was turquoise colored and, after being broken for removal, proved to be about 2.5 cm (1 in.) thick. The remainder of the contents between the turquoise material and the bottom of the drum resembled dirt.

A few pounds of cement were added to the prepared contents but did not account for the volume found. Formation of a similar turquoise material has been observed in heating the nitrate salt surrogate in the lab.

The first indication of a runaway reaction came when smoke was seen from a neighboring test site. Although no inspection of the test apparatus was made, the bunker was entered to retrieve the data and shut down the system. The thermocouples read between 100 and 200°C (212 and 392°F). This is normal for this type of test when the insulation melts leaving shorted wires in the warm, open air close to the hot fixture. The scale also did not give proper readings. The readings were similar to those seen after the readout was turned on but before the connecting cable was connected to the scale. The vacuum pump was running with no apparent problem and was shut down. The test was allowed to cool over the weekend before entry was made. The wood enclosure, black plastic top, and insulation on the sides of the drum were ashes. All wiring insulation and tubing were melted to within 0.6 m (2 ft) of the bunker, a distance of about 1.8 m (6 ft) from the drum. The gutter heater that was previously wrapped around the drum was completely missing, including any wire that may have been imbedded in the insulation.

Disassembling the apparatus was difficult, but clean, since there was no soot or other residue attached to the fittings or drum. All bolts and nuts could be removed, but with some difficulty. The tops of the thermocouples were only metal stubs.

A hacksaw was necessary to remove the lock ring from the drum, since it was partially fused to the drum edge. The lid, although bulged, was mostly undamaged. There were areas along the top of the drum where the melted sample was ejected, leaving an opening less than 2.5 cm (1 in.) down from the top edge and 15 to 20 cm (6 to 8 in.) long in several places. No other part of the drum showed damage except discoloration and warping of the bottom. Removing the heating apparatus was not difficult since the drum was practically empty of material.

Reversing the lid revealed that the three thermocouples and the 1-cm (0.5-in.) stainless steel vent tube were missing. Only one 8-cm (3-in.)-long thermocouple stub remained. This hardware was not found in the drum, leaving the assumption that the hardware melted and was ejected. When the interior heating hardware was removed, the surface of the turquoise material was shiny clean with no debris remaining in the drum.

Removal of the drum from the scale revealed undamaged insulation (six layers) between the drum and the scale, although the foil backing adhered to the scale deck. This was probably caused by a combination of weight and heat. The plywood and 2 × 4-ft platform under the scale were completely gone, leaving the scale sitting in the sand with charcoal in some areas.

The high temperature of the reaction damaged two portions of the apparatus: the heater and balance. The scale was severely damaged in the reaction and had to be replaced. The lower frame was warped about 1 cm (0.5 in.), and the aluminum electrical connector reached a temperature that allowed the metal to soften and curve downward. The heater also was damaged, with a resistance reading of zero. Some soft black material oozed from the joints, which was probably an indication that the interior of the heater exceeded the maximum operating temperature.

Except for the heater, the rest of the heating mechanism seemed undamaged. There was considerable molten (and hardened) metallic material that adhered to the heating tube and slotted casing. Steam cleaning alone was not effective, indicating that the salts had changed into an insoluble material.

### **J-6.2.2 Data Evaluation**

The reaction occurred into the 15th day of testing. The heating ramp or heating rate had been raised in 25°C (77°F) increments from the beginning of Phase 2 of the test. At 425°C (797°F), the heater was plugged directly into the electrical outlet. The drum lost a total of 22.2 kg (49 lb) of sample material.

The temperature profiles were uneventful until the last day (see Figure J-5). Weight loss accelerated with the increase of temperature (see Figure J-6). During the first day of heating, moisture (approximately 40 mL [1.4 oz] of liquid) collected in the vacuum lines. The moisture probably was drawn into the drum through the air intake pipe during the cooling period following Phase 1 of Test 1. After the first day, no liquid was collected in the tubes. A deep reddish-brown film discolored the vacuum tubing. A section of the tube has been saved if needed for analysis.

The expanded view of the last day temperature profiles (Figure J-7) shows that thermal acceleration started about the time the heater was operated without controls. The heater temperature rapidly rose from 479°C (894.2°F) to a maximum of 535°C (995°F) over the next 4 hours, or an increase of 56°C (132.8°F) compared to the maximum temperature of approximately 504°C (939.2°F), which would have corresponded to an increase of 25°C (77°F) over 25 hours, would have resulted from programmed control had the scope of work been followed.

At 535°C (995°F), the center temperature crossed the heater temperature. This event is what EMRTC calls a crossover and is normally followed by a thermal runaway. Heat generated by the reaction is greater than that from the heaters. Soon after crossover, internal pressure removed the drum lid, damaging the thermocouple plugs and wiring and ending collection of thermal data.

A large chunk, 0.9 m (3 ft) long by 0.5 m (1.5 ft) wide and approximately 8 cm (3 in.) thick, of charcoal-colored, low-density material flowed down the outside of the drum and hardened in the sand next to the scales. A sample was taken and sent to the Idaho National Laboratory Site for analysis (see Table J-6 for results).

Table J-6. Anion concentrations of pretest and posttest residue for Test 1: 80 wt% of nitrate salt with 20 wt% of graphite.

Sample	Color	Oxidizer (wt%)		Combustion Product (ppm)	Assumed Inert Surrogate Ingredients (ppm)			
		(nitrate)	(nitrite)	(carbonate)	(chlorine)	(sulfate)	(fluorine)	(phosphate)
Unheated salt surrogate mixture	White	102.0 <sup>a</sup>	77 <sup>a</sup>	144	182	10	102	1,909
Chunks outside drum	Black	0.0	0	20,990	201	11	0	0
Subsurface molten chunk in drum	Off-white	0.2	0	19,960	129	2	90	0
Surface sample in drum	Green	0.2	0	20,160	167	21	96	0

a. Calculated weight percent in original sample based on recipe used to prepare test material.

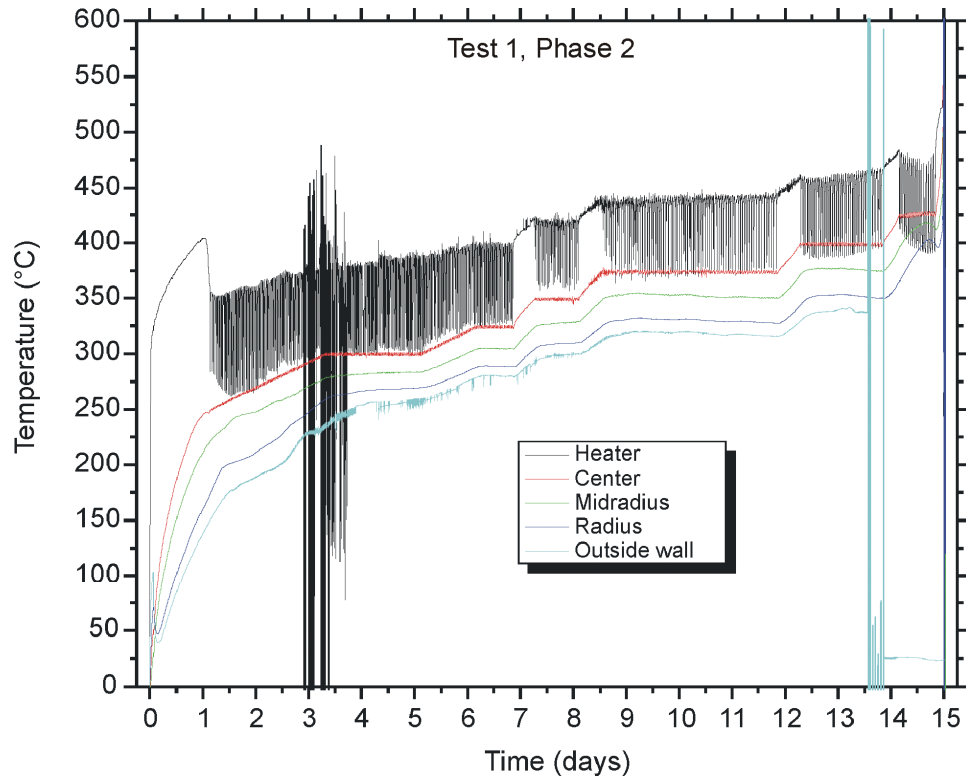


Figure J-5. Temperature profile for Phase 2 testing.

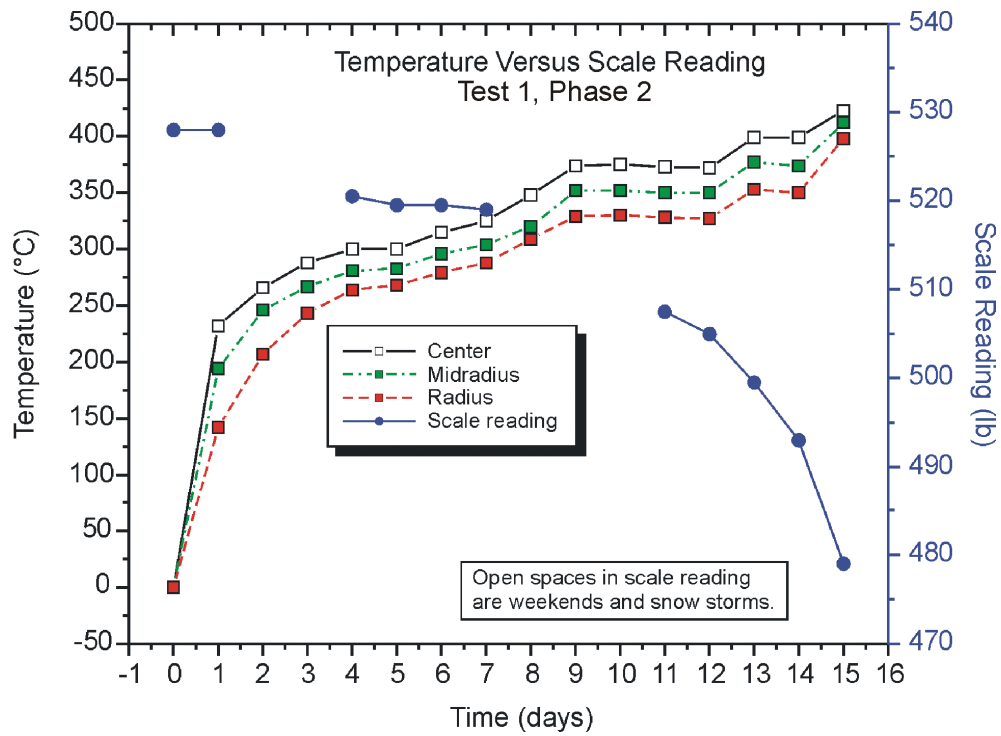


Figure J-6. Temperature profile versus weight lost.

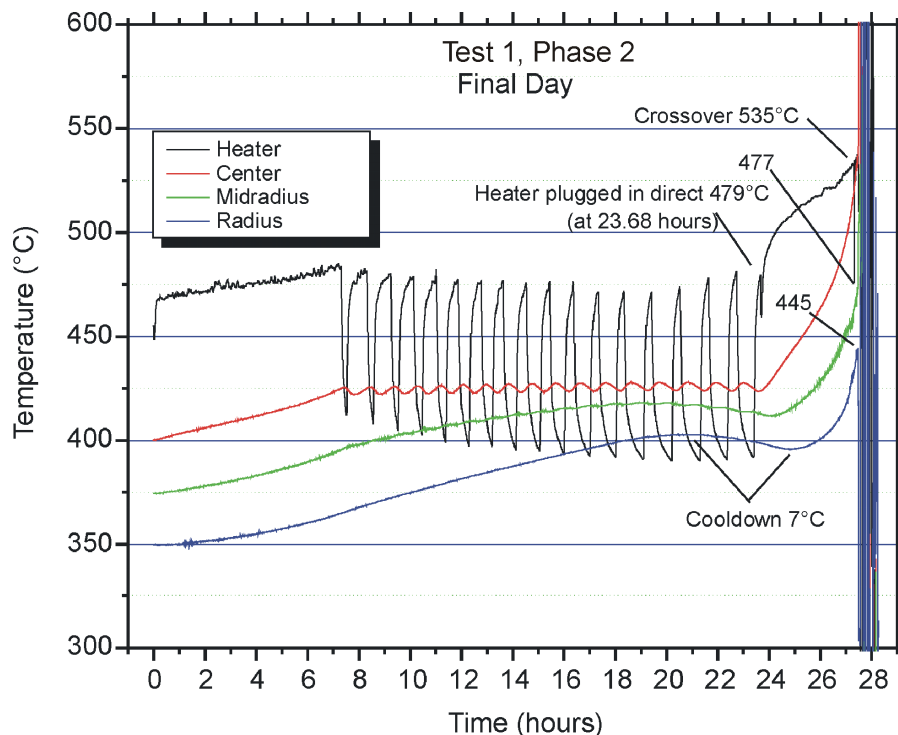


Figure J-7. Temperature profile for last day of test.

### J-6.3 Organic Sludge Test 2

The drum-scale test ran for 3 days before combustion in the insulation damaged the thermocouples and the test was halted. Air drawn in through the inlet appears to have produced some oil combustion.

The drum was heated at a mean rate  $0.3^{\circ}\text{C}$  ( $0.54^{\circ}\text{F}$ )/minute. A temperature profile of the results can be seen in Figures J-8 and J-9. The reading started fluctuating wildly at 70 hours into the test. The cause was unknown but originally was attributed to voltage leakage from the heater or a failing data collection board in the computer.

A review of the temperature profile from the test shows that the heater temperature has wide swings. The center sample temperature was used as the controller, allowing considerable delay between the time the heater started heating and the center temperature finally reached the set point to turn the heater off.

Posttest inspection indicated that oil vapor had collected in the insulation above the lid and then ignited and burned. All that remained of the thermocouple wiring insulation and plugs was black char. Some of the aluminum foil backing on the insulation had also melted or vaporized.

The temperature profile indicated that a reaction probably occurred at the midradius location or that a reaction may have occurred in an area void of temperature probes and was recorded at this location. The radius thermocouple also recorded a steadily increasing temperature rise.

The reaction probably started at approximately 46 hours into the test. Both the midradius and the radius thermocouples recorded an accelerating temperature rise with the midradius temperature peaking at  $478^{\circ}\text{C}$  ( $892.4^{\circ}\text{F}$ ). The radius temperature leveled off at approximately  $212^{\circ}\text{C}$  ( $413.6^{\circ}\text{F}$ ). During this

period of accelerating temperatures, the heater shut off at 54 hours and did not turn on again until 16 hours later.

The test was allowed to continue 21 hours after losing stable temperature readings as seen in Figure J-9. The data were downloaded at the 75-hour mark, which was the only period during the previous 5 hours that the temperature remained stable. The Idaho National Laboratory Site and EMRTC decided to terminate the test at 91 hours since no viable data were being collected.

Disassembly of the drum and heater proved difficult. On bending the lid, a block of whitish material visible toward the bottom of the drum appeared to be all that remained of the sample. With the drum on its side and tied to the bunker, the heating mechanism, with the white block attached, was pulled from the drum using a pickup truck.

The block of material was the diameter of the drum and approximately 25 cm (10 in.) thick. The top 2.5 cm (1 in.) was white, and the lower 23 cm (9 in.) was gray. Samples were collected (using a sledgehammer) and were forwarded to the Idaho National Laboratory Site. The results of the analyses are shown in Table J-7. Disassembly of the heating mechanism from the lid proved impossible until soaked with water. The remaining sample material was water soluble. The thermocouple tips were several inches above the white block.

Table J-7. Anion concentrations of posttest residue for Test 2: 74 wt% of nitrate salt surrogate with 24 wt% of organic sludge surrogate.

Sample	Color	Oxidizer (wt%)		Combustion Product (ppm)	Assumed Inert Surrogate Ingredients (ppm)			
		(nitrate)	(nitrite)	(carbonate)	(chlorine)	(sulfate)	(fluorine)	(phosphate)
Top material	White	93	762	1,386	274	0	82	1,395
Top 1 in. of molten material	White	86	757	1,754	296	0	104	2,013
Center top of heater tube	Off-white	28	1,044	8,494	1,004	0	170	2,288
Bottom 9 in. of molten material	Tan	91	878	1,784	228	0	88	1,659
Bottom material	Gray	89	861	1,987	246	0	99	1,713

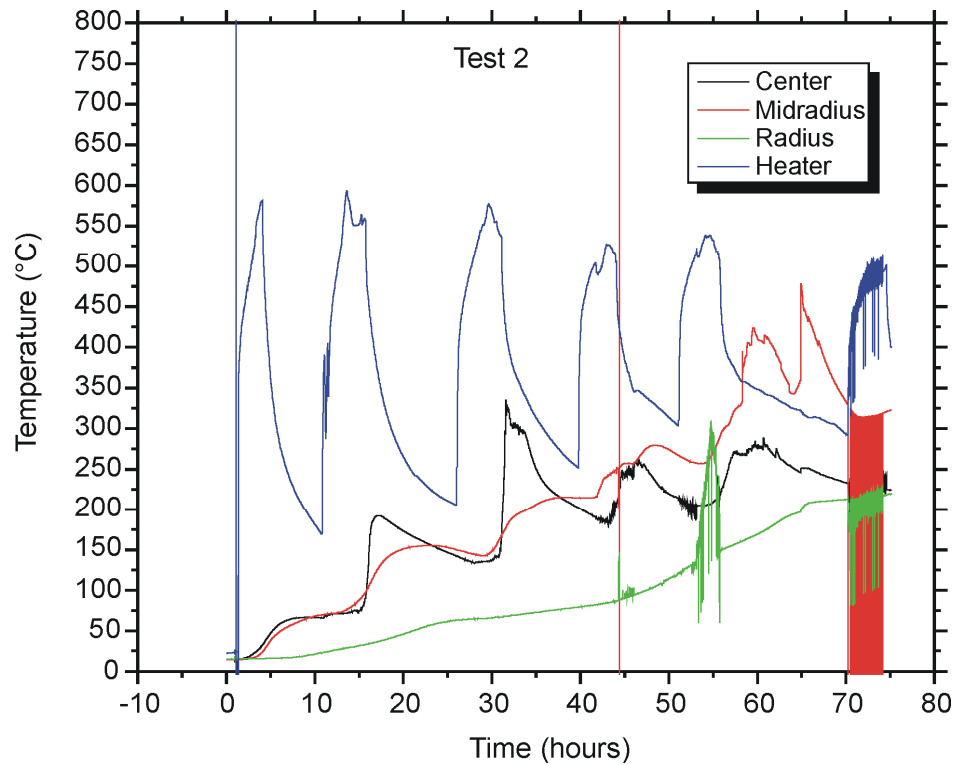


Figure J-8. Temperature profile for heating organic sludge.

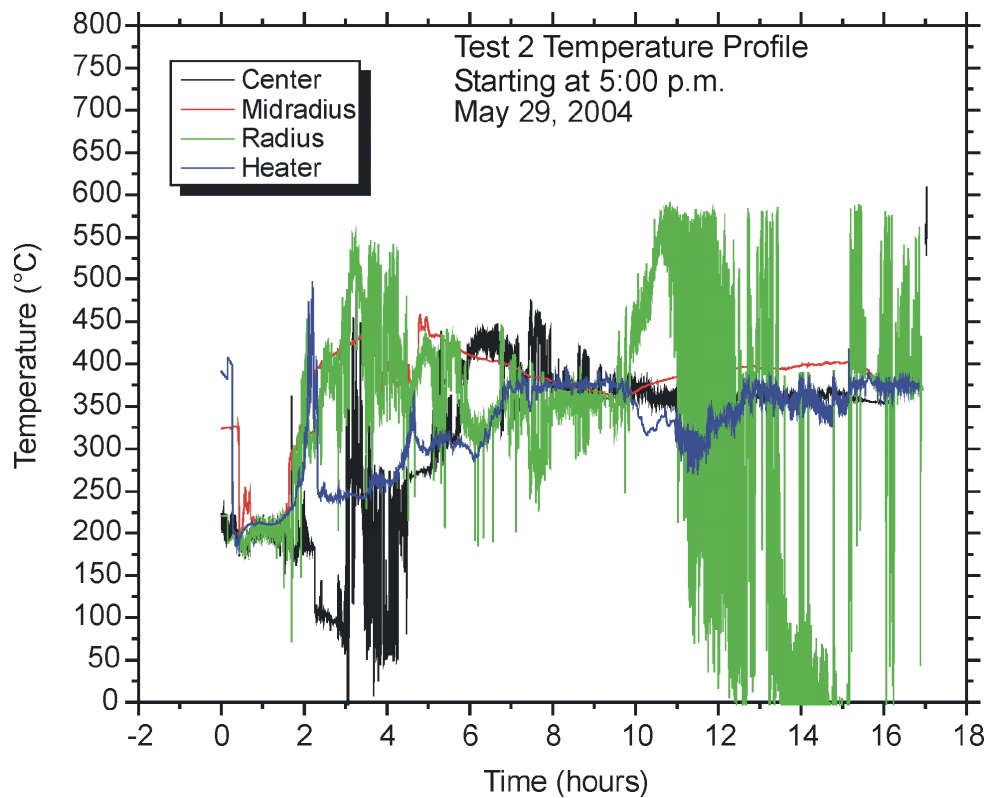


Figure J-9. Temperature profile for organic sludge.

## **J-6.4 Debris Test 3**

### **J-6.4.1 Results**

The sample material ignited at 131 hours. The ignition temperature recorded by the computer logger was 220°C (428°F) at the center thermocouple (see Figures J-10 and J-11). The heating rates are listed in Table J-8. The two peaks shown in the center profile of Figure J-11 should be considered insignificant, since the temperatures were below the liquid temperature of any of the ingredients. Both the air intake and air output hoses were melted off, leaving a source available for fresh air.

The starting temperature of the system was 36°C (96.8°F). At the temperature of reaction, the midradius was 109°C (228.2°F), and the radius was 81°C (177.8°F). Temperature rates also are listed in Table J-9. From the point of reaction until the lid blew off was 72 seconds. Peak temperatures from profiles should be taken with some reservation because data were only recorded every 2 seconds. Note from the temperature profiles that the time interval between reaction at the center and reaction at the radius was 22 seconds. The burning material (deflagration) produced pressure high enough and fast enough to dome the lid before pushing the lid and locking ring upward from the drum. The lid and heating apparatus were found next to the drum in the horizontal position. The heater was undamaged except for some melted insulation on the leads.

A considerable number of absorbent wipes (part of the material used for debris) were found downwind of the test, which would indicate that sample material in the upper part of the drum did not burn before the pressure built up in the drum. Ash from cotton rags was scattered over a 22.9-m (75-ft) radius of the surrounding area.

The scale only showed a weight loss of about 0.68 kg (1.5 lb) of mass until the day before the reaction. Since the reaction was expected to occur at higher temperatures, the site was not visited on Sunday, the day of the explosion. Small weight loss may have been combustion, moisture loss, or effects of heat on the scale. Previous tests indicate that the scale responds to heat by 0.5 +/- 0.23 kg (1 +/- 0.5 lb).

No residue was found on the yellow Cuno filters after the test was terminated. None of the filters or traps contained any residue. The scales, drum, and thermocouples were undamaged by the reaction. The thermocouples were damaged by the impact of the lid and heating apparatus with the ground.

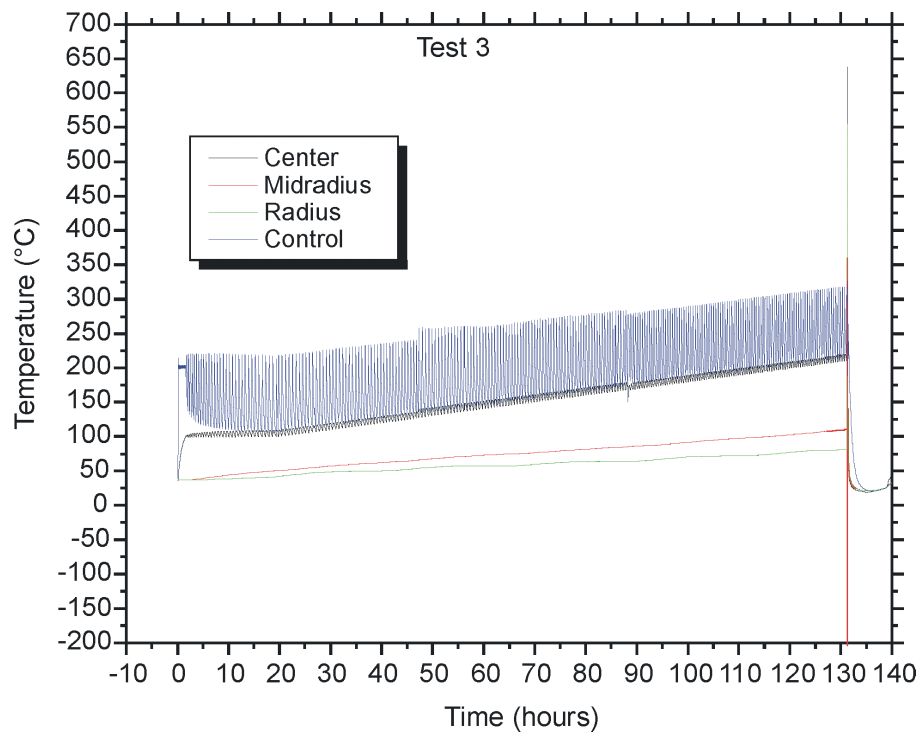


Figure J-10. Temperature versus time for drum content at three positions for Test 3: debris and nitrate salt.

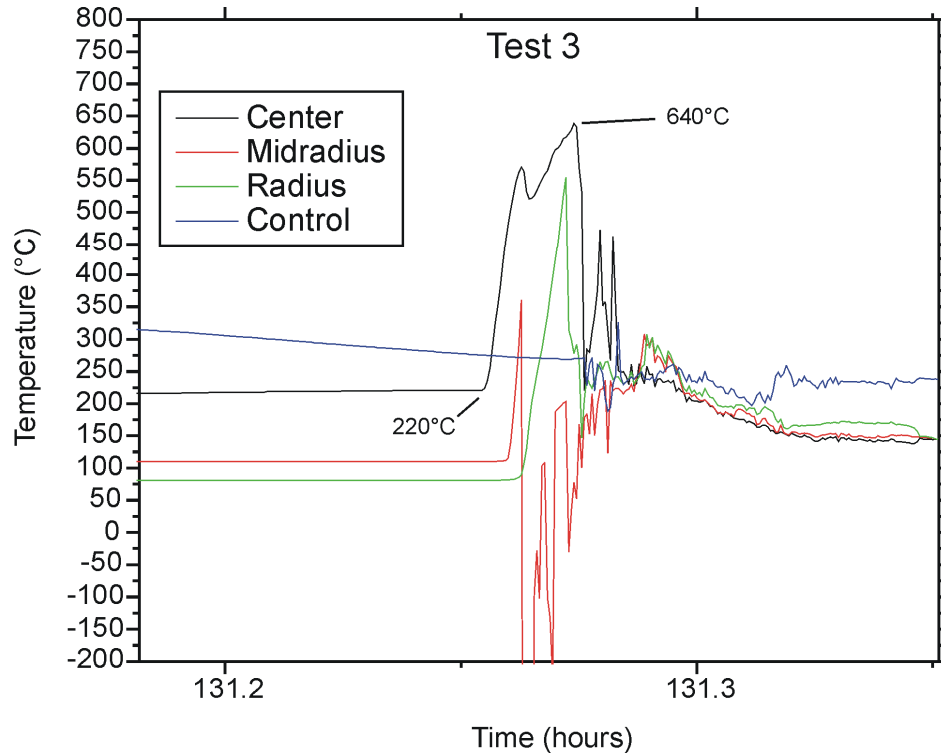


Figure J-11. Expansion of period during greatest reaction for temperature versus time for drum content at three positions for Test 3: debris and nitrate salt.

Table J-8. Thermal summary of drum-scale testing of nitrate salts and surrogates.

Carbon Source / Waste Surrogate Test Number	Heating Center Rate until Stable or Reaction (°C/hour)	Heating Midradius Rate until Stable or Reaction (°C/hour)	Heating Wall Rate until Stable or Reaction (°C/hour)	Heating Mean Rate <sup>a</sup> until Stable or Reaction (°C/hour)	Test Duration (hours)	Maximum Temperature Recorded (°C)	Maximum Mean Temperature <sup>a</sup> (°C)
Graphite powder / 1	3.6	—	0.9	1.5	360	263	210
Graphite powder / 1	—	—	—	—	362	535	486
Organic sludge / 2	3.4	3.4	—	4	75	477	304
Debris / 3	1	1	1	1	131	640	518

a. Average of wall, midradius, and center maximum readings.

Table J-9. Summary of drum-scale reaction.

Carbon Source Waste Surrogate Mixed with Salt Surrogate Mixture (60% sodium nitrate, 30% potassium nitrate, and 10% soluble salts)	Center Rate of Reaction Maximum Temperature (°C)	Wall Rate of Reaction Maximum Temperature (°C)	Maximum Mean Temperature (°C)	Center Rate of Reaction (°C/hour)	Midradius Rate of Reaction (°C/hour)	Wall Rate of Reaction (°C/hour)	Mean Rate of Reaction (°C/hour)	Reaction Time (minute)
Graphite	263	—	210	None	None	None	None	None
Graphite	535	0.9	486	1.5	1.5	1.5	1.5	0.37
Organic sludge	477	—	304	4.0	4.0	4.0	4.0	120.00
Debris	640	1.0	518	1.0	1.0	1.0	1.0	1.20

## J-7. CONCLUSIONS FROM DRUM-SCALE TESTS

Drum-scale tests were performed on mixtures of nitrate salt surrogate with three carbon-containing waste surrogates: organic sludge, graphite, and debris. In each case, the reaction escaped control during the heating process. Reaction rates and temperatures at time of reaction are recorded in Tables J-8 and J-9.

The mixture of nitrate salt surrogate with organic sludge surrogate was the least reactive. While a considerable amount of combustion occurred during the test (and damage to the equipment), the reaction was caused by unexpected release of heated oil (a major component of the organic sludge surrogate) from the drum where it readily combusted with available air. In the subsurface, the amount of available air would be much lower, and the resulting rate of oxidation would be slower. A moderate amount of oxidation in the subsurface could be advantageous since the heat released by oxidation would help heat the subsurface. Gases released through oxidation could be captured by the off-gas treatment system for ISTD.

Consistent with the TGA tests presented in Appendix H, the mixture of nitrate salt surrogate with graphite was more reactive than the mixture containing organic sludge surrogate, and the mixture of nitrate salt surrogate with debris was the most reactive of the three mixtures. During the heating process, the relatively low oxygen environment in the drum allows some of the debris to pyrolyze to carbon. As was shown in the TGA work, nitrate salt surrogate and carbon powder exhibit a strong exotherm with a high heating rate release. The magnitude and duration of the exotherm depend on the heating rate. During Test 3, the majority of the contents of the drum did not react (evidenced by the small weight loss and the uncharred debris expelled from the drum). The cause of deflagration is thought to be the development of a small hot spot, which resulted in a rapid reaction but not an explosion, which generated a large amount of gas rapidly leading to overpressurization of the drum and expelling of most of its contents.

Each time control of the reaction was lost, the heating rate had been raised above the initial set point to speed up the process of heating the material in the drum. Based on the TGA work and these tests, additional testing would need to be conducted before ISTD could be implemented in regions expected to contain nitrate salts and carbon sources. It is possible that uncontrolled reactions could be avoided by lowering the heating rate and lowering the temperature of the heater. It is recognized that slowing heating rate may negatively impact the economics of ISTD; that analysis is beyond the scope of this work.

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## **Appendix K**

### **ISTD of Transuranic Waste Tests: Nonradioactive Surrogates**



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## Appendix K

### ISTD of Transuranic Waste Tests: Nonradioactive Surrogates

The leaching studies for in situ thermal desorption (ISTD) were conducted in two laboratories and are presented in two parts:

- Appendix L—results of tests conducted with radioactive surrogates and waste
- Appendix K—results of tests conducted with nonradioactive surrogates.

The ISTD leach testing of nonradioactive surrogates follows Section 4.2.6 of Yancey et al. (2003).

#### K-1. TEST OBJECTIVES, RATIONALE, AND DEVIATIONS FROM TEST PLAN

The following are objectives of ISTD leach testing with nonradioactive surrogates:

- Evaluate the effect of heating on mobility of nonvolatile contaminants to support contaminant transport modeling for heat-treated waste and soil
- Identify major emissions as waste and soil are slowly heated
- Determine the degree of removal or destruction of hazardous organic contaminants and nitrates from soil and waste as a function of temperature
- Refine and demonstrate the experimental apparatus before testing with radioactive surrogates and waste
- Produce test material for subsequent grouting tests.

These test objectives were met, although time constraints prevented some samples in the heating sequence from leach testing and analysis.

The rare-earth elements were added as nitrate salts or oxides. The natural rare-earth oxide content of the soil and kitty litter also was used for leach testing. Some rare-earth compounds were not available at the time of testing.

Nitrate salts were not subjected to leach tests since they have a very low transuranic content (Shaw, Anderson, and Davis 1993). Salts also remain almost entirely soluble through the temperature range of the testing, thus making partition coefficient ( $K_d$ ) difficult to calculate and apply. Significant decomposition of nitrate salts to alkali oxides in the absence of organics does not occur below approximately 450°C (842°F).

#### K-2. EXPERIMENTAL DESIGN AND PROCEDURES

Three types of surrogates thought to contain high amounts of transuranic contaminants were leach tested: organic sludge surrogate, inorganic sludge surrogate, and soil (see Appendix A for recipes). The soil used in the testing—taken from the Radioactive Waste Management Complex (RWMC) area where the waste and soil reside—was dry and was sieved for uniformity.

Each of the surrogates was spiked with one or several of four rare-earth elements to simulate radionuclides. Four rare-earth elements were used in testing: terbium, lanthanum, cerium, and neodymium. Leach testing used simulated RWMC groundwater containing low concentrations of magnesium sulfate, calcium chloride, sodium nitrate, sodium bicarbonate, potassium bicarbonate, and potassium nitrate (see Appendix A for the recipe).

For all surrogate materials, qualitative observations described the physical characteristics of the waste types as they were heated. Quantitative observations included composition, off-gas concentrations during heating, and  $K_d$ s of rare-earth compounds.

The basic experimental sequence was as follows:

1. Surrogates were prepared and spiked with rare earths
2. Samples were heated to the selected temperature
3. Heat-treated material was leached in simulated groundwater
4. Water was analyzed for rare-earth metals
5. Partitioning was determined by comparing leachate concentration to original solid concentration of rare-earth elements in the surrogate or soil.

## **K-2.1 Preparation and Spiking of Surrogates with Rare Earths**

Hundred-gram quantities of organic sludge surrogate, inorganic sludge surrogate, and soil were prepared (see Appendix A for recipes). Rare-earth elements were then added to the surrogate. In some cases, the natural rare-earth content of soil was used as a tracer because this speciation is different from an added tracer and might resemble more closely the chemical form of contaminants found in the Subsurface Disposal Area. The inductively coupled plasma-mass spectrometry (ICP-MS) technique that was available also could determine leachate concentrations much lower than the inductively coupled plasma or atomic adsorption techniques originally planned.

Lanthanum, cerium, and neodymium were obtained from chemical supply houses as nitrates. Terbium was obtained as an oxide powder from Molycorp, which mines and refines rare-earth elements. Concentrations are shown in Table K-1. Nitrate forms of rare earths were added as aqueous solutions; oxide forms of rare earths were added as dry powders. Solutions of cerium, neodymium, and lanthanum nitrate were added to the inorganic sludge surrogate. Soil naturally contains all of the rare-earth elements selected for this testing. Of those rare earths naturally occurring in soil, lanthanum, cerium, and neodymium occurred in concentrations high enough (parts per million) to be analyzed in the leachate.

These nuclides have been considered or used as surrogates in both lab and field tests (Loomis and Newton 1993; Langer 1984; Loomis and Thompson 1995; Loomis, Zdinak, and Bishop 1997). The nuclides correspond to transuranic radionuclides in oxidation state (+3, +4) and physical movement onto or from soil and have somewhat similar leach properties. Finely divided terbium and cerium were added to the organic sludge to avoid using water and altering the sludge in preparation by drying. For the inorganic sludge surrogate, lanthanum, cerium, and neodymium were added as nitrates (dissolved in water), and terbium was added as an oxide powder.

Table K-1. Concentration of rare earths added to surrogate and soil for partition coefficient leach testing.

Surrogate	Element	Chemical Form of Rare Earth	Amount of Element in Compound (wt%)	Mass of Rare Earth Added to Surrogate (g)	Rare-Earth Concentration in Waste Surrogate as Prepared (mg/kg)
Organic sludge	Terbium	Tb <sub>4</sub> O <sub>7</sub>	85	6.23	18,900
	Cerium	Ce(NO <sub>3</sub> ) <sub>3</sub> 6H <sub>2</sub> O	32	6.41	7,400
Inorganic sludge	Terbium	Tb <sub>4</sub> O <sub>7</sub>	32	20.00	18,800
	Neodymium	Nd(NO <sub>3</sub> ) <sub>3</sub> 6H <sub>2</sub> O	33	10.01	3,600
	Lanthanum	La(NO <sub>3</sub> ) <sub>3</sub> 6H <sub>2</sub> O	32	10.01	3,600
	Cerium	Ce(NO <sub>3</sub> ) <sub>3</sub> 6H <sub>2</sub> O	32	10.00	3,500
Soil	Terbium	Tb <sub>4</sub> O <sub>7</sub>	85	50.12	77,500

H<sub>2</sub>O = water  
 O<sub>7</sub> = oxygen  
 NO<sub>3</sub> = nitrate

Nonradiological (rare-earth) metals were placed on each surrogate matrix and then heated to ISTD process temperatures for the leaching tests that followed. The ability to spike homogeneously and yet leave the surrogate unaltered is difficult because any drying of organic sludge to remove water also will dry off the chlorinated solvents. The slurry method was used for inorganic sludge. The organic sludge and soil used fine powder oxide additions to leave the parent matrix unaltered. Nitrate versions were not used for dry additions as they readily absorb water and tend to clump up, making them difficult to form as a fine powder suitable for addition in a dry form. The following list describes the materials used to make the surrogate types tested:

- **Soil.** Soil used in testing was taken from a noncontaminated area near the RWMC. In two aliquots, 200 g (7.1 oz) of RWMC soil was sieved to less than 75  $\mu$ , 300 g (10.6 oz) was sieved to 75–650  $\mu$ , and then both were combined in a plastic bottle. To this combined sieved soil was added 10 wt% Tb<sub>4</sub>O<sub>7</sub> less than 200  $\mu$  in powdered form. The soil and terbium were then mixed by rolling the plastic bottle.
- **Organic sludge surrogate.** The organic sludge surrogate was prepared by individually weighing the compounds and combining Texaco Regal oil, calcium silicate, and Oil Dri. Then, carbon tetrachloride, trichloroethylene, trichloroethane, and perchloroethylene were added to the first mixture of ingredients and mixed. This mixture was spiked with about 6 g (0.2 oz) of cerium and terbium (as for soil above) to place 1% and 2% of the metals, respectively, in the sludge surrogate to avoid adding water. Organic liquids were added to the absorbent solid with liberal stirring to make 280 g (9.9 oz) of organic sludge (see Appendix A).
- **Inorganic sludge surrogate.** For the inorganic sludge surrogate, the compounds were individually weighed (except for water) and mixed. The appropriate amount of water was calculated—accounting for any differences between the waters of hydration in the recipe and those of the individual chemicals used to prepare the surrogate—and the rare earths terbium, lanthanum, cerium, and neodymium were added to the water as nitrate salts. After the dry ingredients were combined, the appropriate amount of water was added, and the contents were mixed. A mass of 906 g (32 oz) was spiked with equal amounts of three rare-earth elements.

## K-2.2 Heating of Samples

Surrogate and soil samples containing rare-earth elements were heated to selected temperatures in an oxidative atmosphere in ceramic containers open to the atmosphere. Up to 15 g (0.5 oz) of surrogate soil, inorganic sludge surrogate, or organic sludge surrogate samples containing terbium, lanthanum, cerium, and neodymium was placed directly in the ceramic container and then held at temperature (generally 105, 275, or 450°C [221, 527, or 842°F]) for 24 hours. After heating, samples were cooled and weighed.

## K-2.3 Leaching of Simulated Waste and Soil

The solid residues from the organic sludge surrogate, inorganic sludge surrogate, and soil were allowed to cool to room temperature. Samples of material 1–10 g (0.04–0.4 oz) in mass were weighed to the nearest milligram and placed in polypropylene bottles. Enough simulated groundwater was added to each bottle so that the liquid-to-solid ratio was 10 mL (1.4 oz) liquid volume to 1 g (0.04 oz) mass. Generally, a 10-g (0.4-oz) sample was added to 100 mL (3.4 oz) of simulated groundwater. This extractant is the same pH-level-8 groundwater simulant used in testing grout leaching. This simulated groundwater was prepared in a 50-L (13.2-gal) batch (see Appendix A for the recipe).

The samples were maintained at room temperature and stirred or shaken for 24 hours to allow equilibrium to be reached between the sample and solution. Selected samples of each kind of surrogate were leached for an additional 24 hours; some of those samples showed concentrations similar to those for the first leach (see Figures K-1, K-2, and K-3).

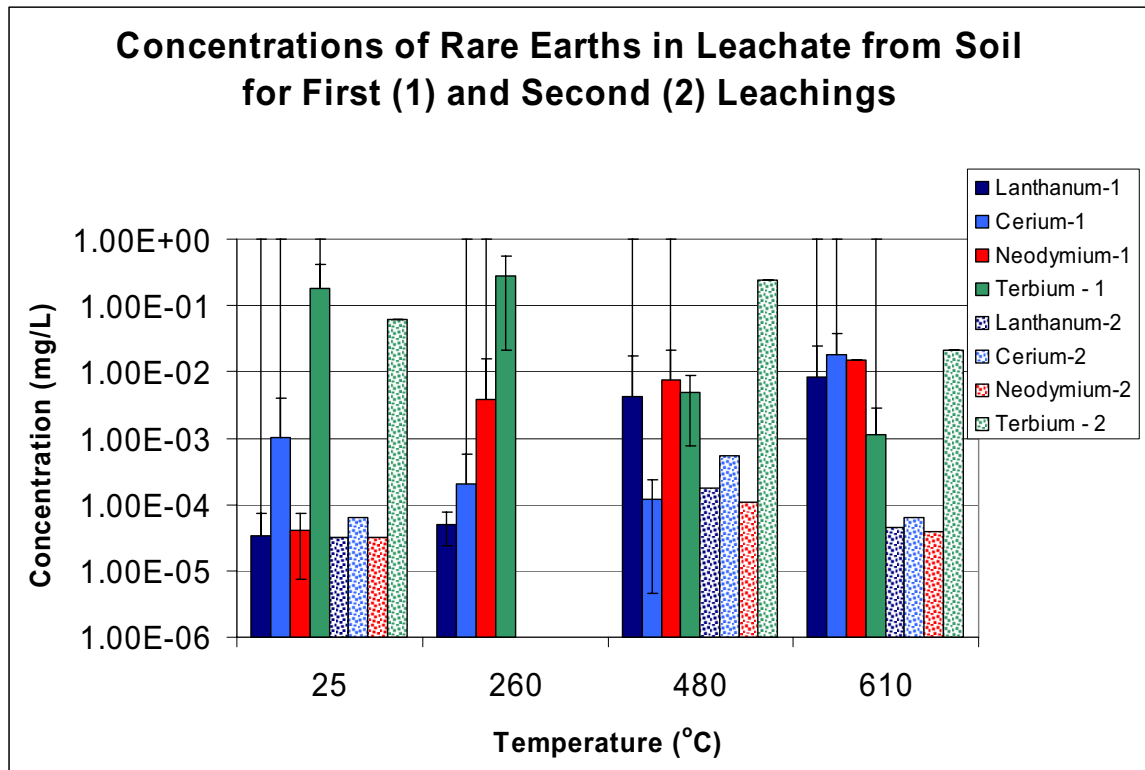


Figure K-1. Concentrations of rare earths in leachate from soil for first and second leachings.

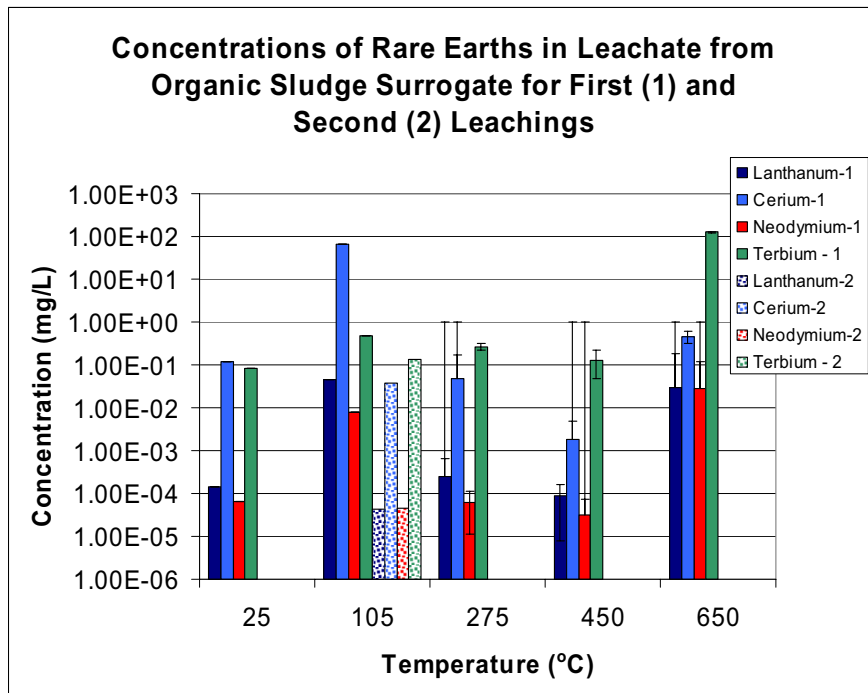


Figure K-2. Concentrations of rare earths in leachate from organic sludge surrogate for first and second leachings.

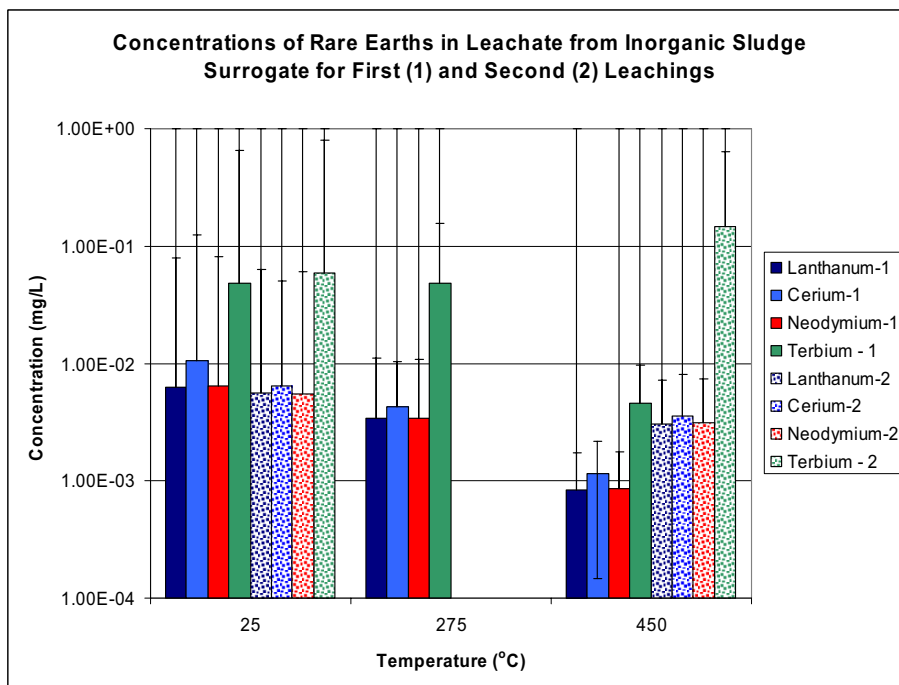


Figure K-3. Concentrations of rare earths in leachate from inorganic sludge surrogate for first and second leachings.

At the end of the equilibration period, liquid was decanted from container and filtered through glass fiber filters in ceramic Gooch crucibles. The solid material on the filter and remaining in the bottle was dried and weighed. The groundwater was submitted for analysis of rare-earth elements and anions.

## **K-2.4 Analyzing Water for Rare-Earth Metals**

Liquid leachate samples for rare-earth analysis were acidified before analysis. The concentrations of rare earths in the filtered liquid were measured by ICP-MS (Thermo Electron Jarell Ash Model X-7). The ICP-MS unit was calibrated using National Institute for Standards and Technology (NIST) nitric acid solutions of the respective rare-earth elements. None of the samples required dilution before ICP-MS analysis.

Anions, including nitrate, were measure by ion chromatograph (DX-500 by Dionex). Components of the Dionex system are a gradient pump (GP50), an electrochemical detector (ED40), and a thermal compartment (AS50). Samples were loaded using a six-port valve (9750E-033 by Rheodyne). A 25- $\mu$ L loop made from polyether-ether-ketone tubing was fitted to the six-port valve. Data were acquired and instruments were controlled by a personal computer with chromatography software (PeakNet).

An eluent generator (Dionex EG40) also was used on the DX-500. The eluent generator was equipped with a cartridge (EGC II-KOH) that produced potassium hydroxide eluents. An analytical column (Dionex AS17 IonPac; 43,250 mm) made ionic separations. A guard column (AG17; 4,350 mm) was also present. Eluent concentrations through the columns were 10 mM for 0 to 3 minutes, 10 to 15 mM for 3 to 5 minutes, 15 to 25 mM for 5 to 8 minutes, 25 to 30 mM for 8 to 12 minutes, and 10 mM for 12 to 15 minutes.

## **K-2.5 Chemicals, Solutions, and Samples**

All standards and samples were prepared and diluted using 18 M $\Omega$ /cm or greater water. Standards were prepared using Dionex seven-anion standard. The ion chromatography unit was calibrated by NIST-traceable standard anion solutions of sodium or potassium salts. Original concentrations of the standard were 20 mg/L of fluoride, 30 mg/L of chloride, 100 mg/L of nitrite, 100 mg/L of bromide, 100 mg/L of nitrate, 150 mg/L of phosphate, and 150 mg/L of sulfate. Other standards were prepared using serial dilutions of the original.

Some of the inorganic sludge extracts had to be diluted because of high nitrate concentration. The prepared concentration of rare-earth elements in each surrogate or soil was used as the solid concentration before leaching. Replicates verified homogeneity of the rare-earth spike.

## **K-2.6 Determining Partition Coefficient Partitioning**

A  $K_d$  was determined for heated and nonheated samples of surrogates and soil. The  $K_d$  is intended to measure partitioning between a solid and liquid rather than diffusion over time. Partitioning was determined by comparing to original solid concentrations of rare-earth elements in the surrogate or soil-to-liquid concentration. The ratio of solid over liquid is  $K_d$ . The calculation is described in Section K4, "Data Management, Analysis, and Interpretation."

## **K-3. EQUIPMENT AND MATERIALS**

Materials for rare-earth leaching are also described in Section 4 of Yancey et al. (2003). Lanthanum, cerium, and neodymium were obtained from chemical supply houses as nitrates. Terbium as

an oxide powder came from Molycorp, which mines and refines rare-earth elements. Concentrations used are shown in Table K-1. Nitrate forms of rare earths were added as aqueous solutions; oxide forms of rare earths were added as dry powders.

Photographs of the tube furnace that heated the samples are shown in Figure K-4. (In Figure K-4, the tube in which the sample is placed is shown laying in the open furnace on the left; the heating element that runs the length of the tube is visible in the lid of the open furnace.) Chemicals used in testing were commercial and laboratory grade. The ICP-MS (a Perkin Elmer) determined the concentrations of rare earths present in solutions. Ion chromatography (by Dionex) determined the concentrations of anions in the solutions.



Figure K-4. Tube furnace equipment used for testing.

## K-4. DATA MANAGEMENT, ANALYSIS, AND INTERPRETATION

Data were collected from instruments and their attached computers with analysis on spreadsheets. Signal response was compared with known standards to determine relative concentrations. Balances were calibrated by calibration services and checked with check weights periodically. Analytical instruments have internal and external calibrations. The primary calculation in leaching solids that are not in cylindrical form is converting the concentrations before and after into  $K_d$  using Equation (K-1):

$$K_d = [M]_{\text{solid}}/[M]_{\text{solution}} \quad (\text{K-1})$$

where:

$[M]_{\text{solid}}$  = mass of contaminant of concern in the soil or solid form in units of milligram per kilogram

$[M]_{\text{solution}}$  = mass of contaminant of concern in leach solution in units of milligram per liter.

In dilute solutions, a plot of  $[M]_{\text{solution}}$  as a function of  $[M]_{\text{solid}}$  should be linear. A regression analysis is performed on the plot, and the slope =  $K_d$ . A full  $K_d$  analysis was beyond the scope of this work; measurements were taken at a single solid concentration. The data reported in this appendix provide a first approximation of the  $K_d$  for the rare earths tested.

Quality-control samples are 10–20% of the sample load and included:

- Blanks—leach solution without any solid, and sludge or soil with no spikes
- Standards—known metal concentration solutions and NIST standard material
- Spikes—additional analyte to a sample
- Replicates—leaching multiple portions of the same solid in the same manner.

Standard deviations on replicates were generally within 10%. Spikes and replicates indicated no significant interferences from the sample matrix other than distribution of spike in the organic sludge matrix. Detection limits for ICP-MS are listed in Table K-2. These are determined by taking the root mean square of readings from blanks. This combines the noise of the instrument and nonanalyte contents of the solution. The two batches of rare-earth-element samples had similar detection limits.

Table K-2. Inductively coupled plasma-mass spectrometry quality control detection limit and mean percent error for rare-earth elements.

Detection Limit	Lanthanum	Cerium	Neodymium	Terbium
	(ppb)			
First set	0.003	0.005	0.010	0.003
Second set	0.004	0.005	0.006	0.005
	(%)			
Mean error	$0.9 \pm 4.2$	$3.6 \pm 4.3$	$2.4 \pm 4.3$	$3.6 \pm 5.1$

## K-5. RESULTS AND CONCLUSIONS

Results of the tests are presented below with qualitative observations followed by quantitative observations and then conclusions.

### K-5.1 Qualitative Observations

Each surrogate changed in color and texture on heating. The organic sludge surrogate samples lost progressively more weight as heating temperature increased (see Figure K-5). Chemical changes were also apparent in that the residue after heating appeared different in both color and texture from the original material, suggesting that weight loss was caused by more than loss of water.

The soil turned from a light tan to a reddish color as it reached sintering temperatures above 500°C (932°F). Soil clays and iron gave an orange color on heating through the approximately 150°C (302°F) range and then began to darken at approximately 200°C (392°F) to a dark-reddish brown at 300°C (572°F) and finally a light brown at 450°C (842°F).

The inorganic sludge became slightly lighter; some of the nitrate salts crystallized as they were heated. On heating to 275°C (527°F), the material became similar in appearance to dry clay soil. An orange tint appeared gradually as temperature increased.

The organic sludge changed from green to light brown at 105°C (221°F), turning darker as oil carbonized at 275°C (527°F) and 450°C (842°F). A black residue was deposited in the tube at greater than 200°C (392°F), finally producing a light ash following 450°C (842°F).

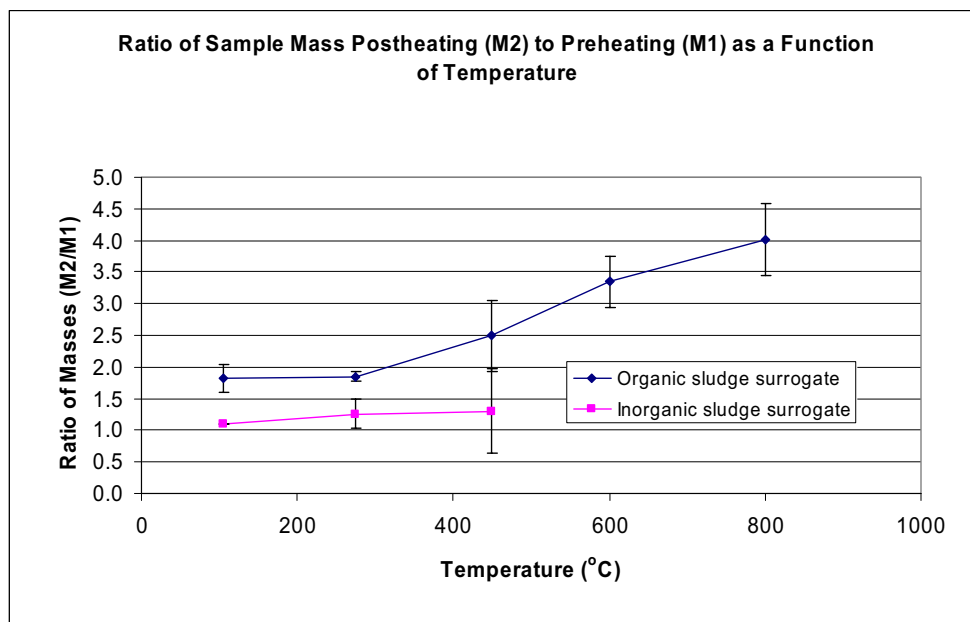


Figure K-5. Mass loss in surrogates as a function of ISTD treatment temperatures.

## K-5.2 Quantitative Observations

The sections below describe the quantitative results and conclusions for leaching of nitrates and rare-earth elements from heated surrogates and soils.

## K-5.3 Soil

The measured lanthanum, cerium, and neodymium occurred naturally in the soil, while the terbium was added as an oxide to the soil. The  $K_d$ s for lanthanum, cerium, and neodymium remained fairly constant as temperature increased (see Figure K-6), while the  $K_d$  for terbium appeared to increase as the temperature increased above 275°C (527°F); there are no statistical differences among the four rare earths at 610°C (1,130°F). The mean  $K_d$  was on the order of  $1E+06$  for most of the rare earths and temperatures; the 95% confidence intervals for most of these same data were the same order of magnitude as the mean (see Table K-3).

Table K-3. Measured concentrations of rare earths in leach solutions and calculated partition coefficient for soil.

Temperature (°C)	Value	Concentration (mg/L)				Partition Coefficient (mL/g)			
		Lanthanum	Cerium	Neodymium	Terbium	Lanthanum	Cerium	Neodymium	Terbium
25	Mean	3.35E-05	1.02E-03	4.03E-05	1.81E-01	1.20E+06	5.65E+05	7.92E+05	7.18E+05
	Standard deviation	2.46E-05	1.88E-03	2.07E-05	1.43E-01	5.94E+05	4.14E+05	3.89E+05	5.88E+05
	Confidence interval	3.92E-05	3.00E-03	3.29E-05	2.27E-01	9.45E+05	6.59E+05	6.19E+05	9.36E+05
260	Mean	5.00E-05	2.01E-04	3.78E-03	2.84E-01	7.24E+05	7.70E+05	1.05E+06	4.06E+05
	Standard deviation	1.63E-05	2.36E-04	7.48E-03	1.65E-01	2.67E+05	8.02E+05	6.09E+05	2.51E+05
	Confidence interval	2.60E-05	3.75E-04	1.19E-02	2.63E-01	4.25E+05	1.28E+06	9.69E+05	3.99E+05
480	Mean	4.30E-03	1.20E-04	7.51E-03	4.85E-03	1.27E+06	6.97E+05	1.84E+06	2.25E+07
	Standard deviation	8.47E-03	7.26E-05	8.65E-03	2.56E-03	8.57E+05	4.17E+05	3.04E+05	8.61E+06
	Confidence interval	1.35E-02	1.15E-04	1.38E-02	4.07E-03	1.36E+06	6.63E+05	4.84E+05	1.37E+07
610	Mean	8.52E-03	1.80E-02	1.50E-02	1.14E-03	2.17E+06	2.97E+06	2.63E+06	2.02E+08
	Standard deviation	9.80E-03	1.20E-02	0.00E+00	1.12E-03	7.20E+05	6.60E+05	0.00E+00	1.57E+08
	Confidence interval	1.56E-02	1.91E-02	0.00E+00	1.78E-03	1.15E+06	1.05E+06	0.00E+00	2.49E+08

Note: Green shading indicates that two-third or more of data used in the calculation were below detection limit. For the value of those samples below detection limit, the detection limit was used.

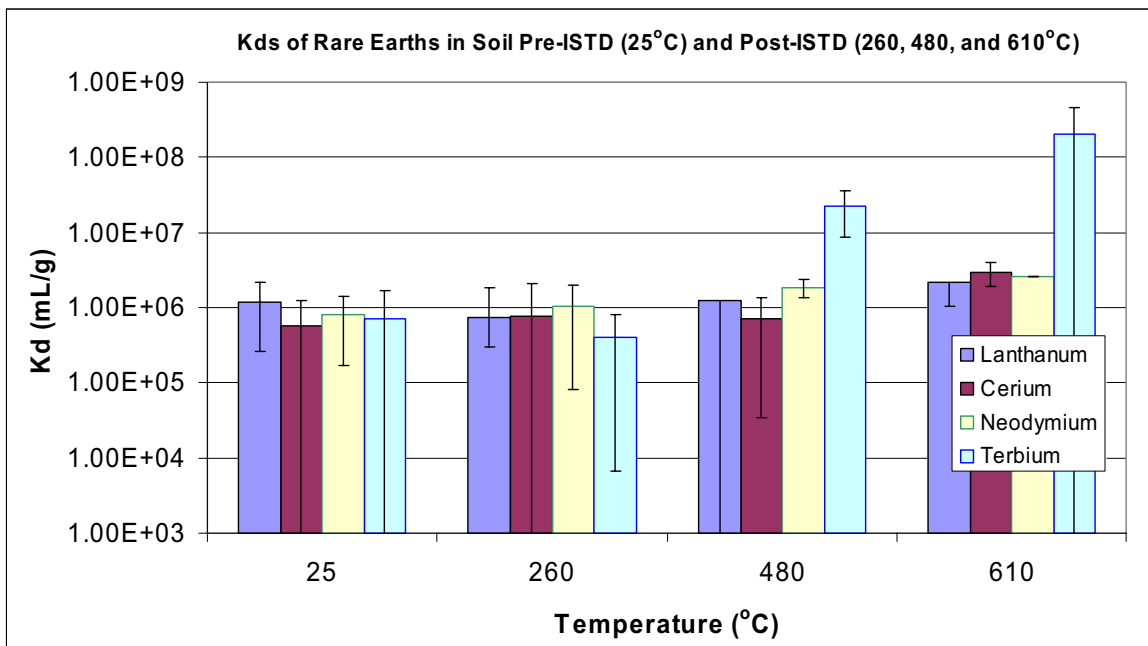


Figure K-6. Partition coefficients of rare earths from soil.

### K-5.4 Inorganic Sludge Surrogate

The lanthanum, cerium, and neodymium (as nitrates) and terbium (as an oxide) were added to the inorganic sludge surrogate. The  $K_d$ s for lanthanum, cerium, neodymium, and terbium remained fairly constant as the temperature increased (see Figure K-7). The mean  $K_d$  was on the order of  $1E+06$  for most rare earths and temperatures; the 95% confidence intervals for these same data were the same order of magnitude or one order larger than the mean (see Table K-4).

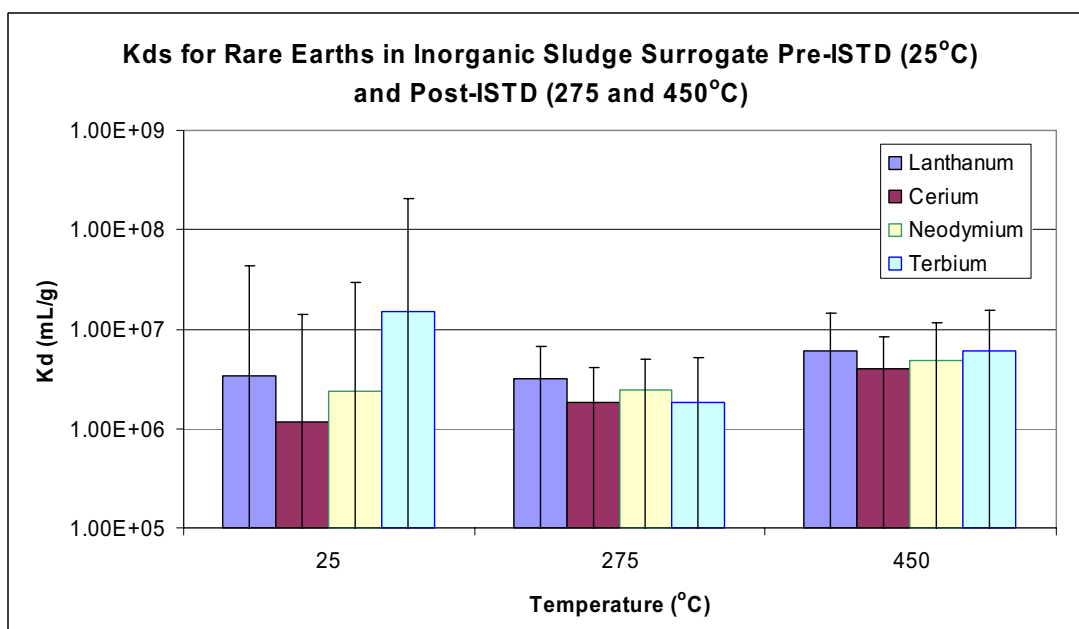


Figure K-7. Partition coefficients for rare earths from inorganic sludge surrogate.

Table K-4. Measured concentrations of rare earths in leach solutions and calculated partition coefficients for inorganic sludge surrogate.

Temperature (°C)	Value	Concentration (mg/L)				Partition Coefficient (mL/g)			
		Lanthanum	Cerium	Neodymium	Terbium	Lanthanum	Cerium	Neodymium	Terbium
25	Mean	6.26E-03	1.05E-02	6.50E-03	4.83E-02	3.40E+06	1.17E+06	2.35E+06	1.51E+07
	Standard deviation	8.15E-03	1.27E-02	8.34E-03	6.75E-02	4.43E+06	1.42E+06	3.02E+06	2.11E+07
	Confidence interval	7.32E-02	1.14E-01	7.49E-02	6.07E-01	3.98E+07	1.27E+07	2.71E+07	1.89E+08
275	Mean	3.43E-03	4.31E-03	3.45E-03	4.80E-02	3.19E+06	1.82E+06	2.48E+06	1.84E+06
	Standard deviation	4.73E-03	3.74E-03	4.68E-03	6.74E-02	2.25E+06	1.43E+06	1.57E+06	2.06E+06
	Confidence interval	7.53E-03	5.94E-03	7.45E-03	1.07E-01	3.57E+06	2.28E+06	2.50E+06	3.28E+06
450	Mean	8.37E-04	1.16E-03	8.67E-04	4.55E-03	6.02E+06	3.99E+06	4.85E+06	6.07E+06
	Standard deviation	3.65E-04	4.08E-04	3.71E-04	2.07E-03	3.45E+06	1.71E+06	2.74E+06	3.72E+06
	Confidence interval	9.07E-04	1.01E-03	9.21E-04	5.14E-03	8.58E+06	4.25E+06	6.82E+06	9.25E+06

### K-5.5 Organic Sludge Surrogate

Lanthanum, cerium, and neodymium (as nitrates) and terbium (as an oxide) were added to the organic sludge surrogate. The  $K_d$ s for lanthanum, cerium, neodymium, and terbium appear to increase as the temperature increases (see Figure K-8). (In Figure K-8, error bars are not present for the 25 and 105°C data because no replicates were taken for these points.) However, the 95% confidence interval for each of the rare earths at 650°C (1,202°F) exceeds the value of the mean. The mean  $K_d$ s spanned seven orders of magnitude ( $10^2$  to  $10^9$ ); the values of the 95% confidence intervals for these same data were the same order of magnitude or larger than the mean (see Table K-5).

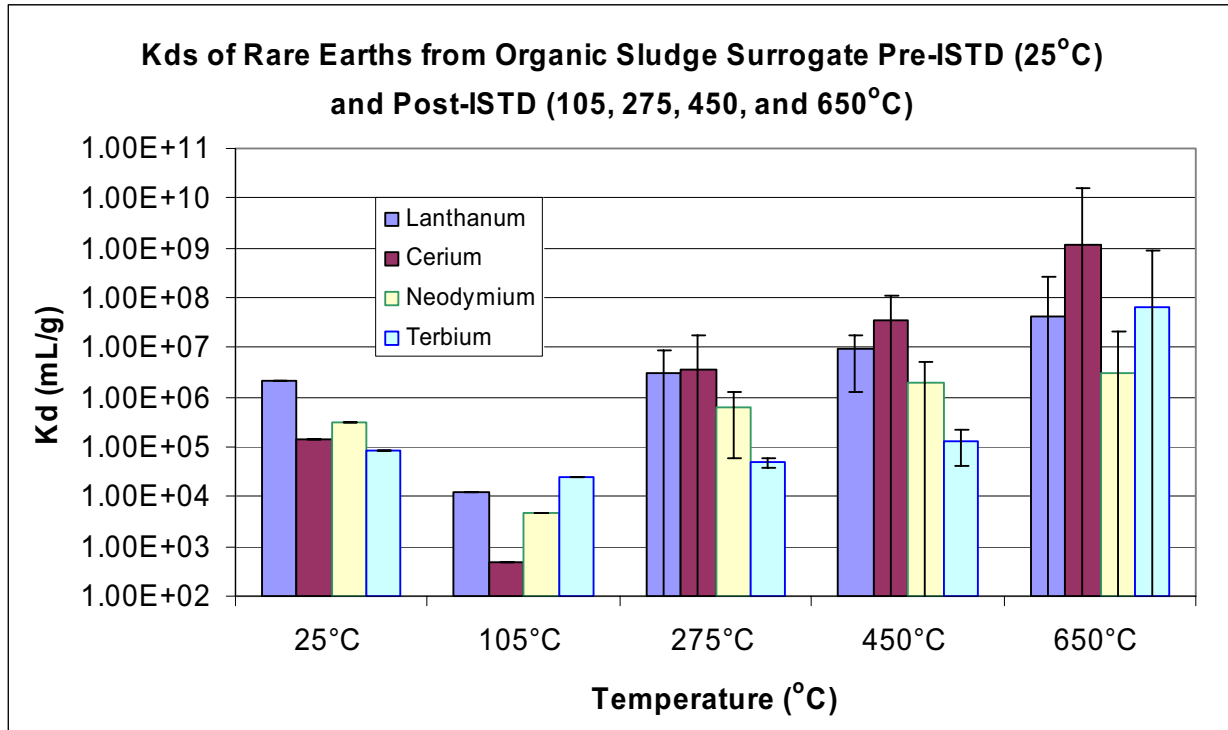


Figure K-8. Partition coefficients for rare earths from organic sludge surrogate.

Table K-5. Measured concentrations of rare earths in leach solutions and calculated partition coefficients for organic sludge surrogate.

Temperature (°C)	Value	Concentration in Leachate (mg/L)				Partition Coefficient (mL/g)			
		Lanthanum	Cerium	Neodymium	Terbium	Lanthanum	Cerium	Neodymium	Terbium
25	Mean	1.40E-04	1.22E-01	6.40E-05	8.33E-02	2.14E+06	1.37E+05	3.13E+05	8.16E+04
	Standard deviation	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Confidence interval	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
105	Mean	4.49E-02	6.38E+01	7.70E-03	4.82E-01	1.21E+04	4.74E+02	4.72E+03	2.56E+04
	Standard deviation	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Confidence interval	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
275	Mean	2.53E-04	4.95E-02	6.13E-05	2.62E-01	3.12E+06	3.74E+06	6.54E+05	4.81E+04
	Standard deviation	1.67E-04	4.82E-02	2.01E-05	1.94E-02	2.27E+06	5.63E+06	2.40E+05	3.73E+03
	Confidence interval	4.15E-04	1.20E-01	5.00E-05	4.83E-02	5.64E+06	1.40E+07	5.97E+05	9.27E+03
450	Mean	8.60E-05	1.84E-03	3.10E-05	1.31E-01	9.48E+06	3.47E+07	2.01E+06	1.35E+05
	Standard deviation	3.14E-05	1.17E-03	1.65E-05	3.34E-02	3.33E+06	3.00E+07	1.18E+06	3.77E+04
	Confidence interval	7.81E-05	2.91E-03	4.10E-05	8.30E-02	8.27E+06	7.45E+07	2.93E+06	9.36E+04
650	Mean	2.95E-02	4.64E-01	2.85E-02	1.24E+02	4.15E+07	1.19E+09	3.03E+06	6.69E+07
	Standard deviation	1.77E-02	1.63E-02	1.06E-02	3.35E-02	2.49E+07	1.60E+09	2.03E+06	9.45E+07
	Confidence interval	1.59E-01	1.47E-01	9.50E-02	3.01E-01	2.23E+08	1.44E+10	1.82E+07	8.49E+08

## K-6. CONCLUSIONS

Overall, heating does not appear to affect the retention of rare earths in the surrogates and soil tested. The mean  $K_d$  is around  $1E+06$  for lanthanum, cerium, neodymium, and terbium over a temperature range of 25 to 450°C (77 to 842°F) for soil and inorganic sludge surrogate. The magnitude of the  $K_d$ s ranges from  $10^2$  to  $10^9$  for all the surrogates, soil, and rare-earth elements.

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## **Appendix L**

### **ISTD of Transuranic Waste Tests: Radioactive Surrogates and Waste**



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## **Appendix L**

### **ISTD of Transuranic Waste Tests: Radioactive Surrogates and Waste**

The leaching studies for in situ thermal desorption (ISTD) were conducted in two laboratories and are presented in two parts:

- Appendix L—results of tests conducted with radioactive surrogates and waste
- Appendix K—results of tests conducted with nonradioactive surrogates.

In situ thermal desorption is a possible treatment of buried waste within the Subsurface Disposal Area. Four temperatures—ambient (~21–24°C [69.8–75.2°F]), 105, 275, and 450°C (221, 527, and 842°F)—were evaluated in bench-top tests using surrogate and waste in a tube furnace. At lower temperatures, this technique has the potential to remove significant quantities of volatile and semivolatile organics. At higher temperatures, this technique has the potential to degrade nitrate salts and some of the organic compounds. This testing was structured to focus on evolution of nitrogen and carbon gases, organochlorine compounds, and volatilization or fixation of actinides as a result of heating.

#### **L-1. TEST OBJECTIVES, RATIONALE, AND DEVIATIONS FROM TEST PLAN**

The following are objectives of this portion of the leach testing:

- Estimate the effect of ISTD on the leachability of radionuclides in soil, organic sludge, nitrate salt, and inorganic sludge
- Determine whether significant amounts of nitrates, organochlorines, actinides, or all three are volatilized from Pad A salt and organic sludge when heated
- Produce test material for subsequent grouting tests.

The tests were performed on actinide-spiked surrogates of organic sludge, inorganic sludge, and soil and on Pad A salt and organic sludge waste composite samples retrieved from Pit 9.

##### **L-1.1 Equipment and Materials**

The surrogate was prepared by spiking clean Radioactive Waste Management Complex lakebed soil, organic sludge surrogate, and inorganic sludge surrogate with known amounts of the actinides uranium, plutonium, neptunium, and americium. The soil originated at the lakebed sites near Big Southern Butte, the same location as the soil historically used for backfill in pits and trenches. It was sieved to 50 mesh and dried at room temperature before use. The organic sludge surrogate and inorganic sludge surrogate were supplied to the Reactor Technologies Complex (RTC) labs by the project. Uranium was weighed out as uranium oxide, nitrate, and water. The plutonium, neptunium, and americium were diluted from stock solutions that were characterized by gamma-ray counting at the Radiation Measurements Laboratory at RTC. Slurries were prepared with thorough mixing, followed by drying as necessary to produce a weighable waste matrix. The organic sludge surrogate was slurried with methanol.

Actinide concentrations in the surrogates were selected based on isotope and median concentration data from a recent analysis of waste from the Idaho National Laboratory Site (Blackwood and Hoffman 2004). Concentrations of natural uranium, Pu-239, Np-237, and Am-241 were as close as possible to the medians specified, considering both instrument detection limits for leachate analysis and radiological control practices.

Small samples (1–4 g [0.04–0.1 oz]) of surrogate or waste were placed in a quartz boat, which was placed inside the quartz tube of a tube furnace. The furnace was located in a radiologically controlled fume hood. This sample was then heated to the test temperature and held there for 4 hours. Airflow of 10 mL/minute was pulled through the quartz tube by a rotoflex pump during heating, although at high temperatures, flow was sometimes restricted by the evolution of large amounts of volatilized oil from the organic sludge. As sample gas exited the downstream side of the furnace, it passed through a 0.2- $\mu$ m filter to trap actinides, followed by a mildly basic bubbler solution to trap acidic anions such as nitrate. Samples were held at temperature for 4 hours. Weight loss caused by heating was measured as the mass change following temperature treatment.

Gas analyses used gas chromatography (an HP5890 GC). The gas chromatography (GC) device was equipped with two detectors to analyze the suite of requested analytes. A splitter allowed one injection to measure analytes with both detectors. Organochlorine constituents were analyzed using an electron capture detector (ECD). As organic sludge is heated, organic constituents—including organochlorines—would eventually volatilize and then be detectable in the gas stream. The ECD was calibrated using carbon tetrachloride. The carbon monoxide, carbon dioxide, nitrous oxide, and sulfur dioxide were analyzed using a thermal conductivity detector (TCD).

## **L-2. EXPERIMENTAL DESIGN AND PROCEDURES**

Tests were conducted with surrogate spiked with radionuclides and samples of waste (already containing radionuclides). The recipes for the nonradiological components of the surrogates prepared are shown in Tables A-3 (organic sludge surrogate) and A-4 (inorganic sludge surrogate) of Appendix A. Surrogate soil and waste were spiked with radionuclides as follows:

- Soil—A slurry was made using 100.95 g (3.6 oz) of Radioactive Waste Management Complex soil, sieved to 50 mesh. To this was added 1.4 mL (0.05 oz) of 99.6- $\mu$ Ci/mL Pu-239 solution, 3.5 mL (0.1 oz) of 63.9- $\mu$ Ci/mL Am-241, 0.37 mL (0.01 oz) of 41.4- $\mu$ Ci/mL Np-237, and 172 mg (0.006 oz) of uranium oxide, nitrate, and water. These were added to the slurry in small aliquots with 1 minute of stirring between additions. This was then dried overnight in a vacuum oven at low heat. The final concentrations were 1,381 nCi/g (22.6 ppm) of plutonium; 2,216 nCi/g (0.65 ppm) of americium; 152 nCi/g (210 ppm) of neptunium; and 808 ppm of uranium.
- Organic sludge surrogate (Batch 1)—The organic sludge surrogate was prepared as described in Table A-3 of Appendix A. The actinide spikes were as for soil above, without neptunium. The spike solution was prepared in a minimum volume of 0.02 *M* hydrogen nitrate, diluted by 50% with methanol. This solution was then doubled in volume again with mineral oil and a few drops of surfactant to make the phases miscible, but without complexing the actinides. The final ~5 mL (0.2 oz) was added to the 98.8 g (3.5 oz) of organic sludge with liberal stirring. Final concentrations were 1,411 nCi/g (23.1 ppm) of plutonium; 2,262 nCi/g (0.66 ppm) of americium; and 825 ppm of uranium.
- Organic sludge surrogate (Batch 2)—This batch was prepared similarly to above, as 39.9 g spiked with 0.56 mL of 99.6- $\mu$ Ci/mL plutonium, 1.4 mL of 63.9- $\mu$ Ci/mL americium, and 68.8 mg of uranium oxide, nitrate, and water. The resulting concentrations were 1,397 nCi/g (22.8 ppm) of plutonium; 2,241 nCi/g (0.66 ppm) of americium; and 817 ppm of uranium.

- Inorganic sludge (Batch 1)—The inorganic sludge surrogate was prepared as described in Table A-4 of Appendix A. This was slurried with water in the same manner as the soil above. A mass of 100.8 g (3.6 oz) was spiked with the same amounts of actinides as for the soil above, resulting in 1,383 nCi/g (22.6 ppm) of plutonium; 2,219 nCi/g (0.65 ppm) of americium; 152 nCi/g (210 ppm) of neptunium; and 809 ppm of uranium. This was dried in the same manner as the soil and then reconstituted with the appropriate amount of water before grouting.
- Inorganic sludge surrogate (Batch 2)—This was prepared similarly to the above, but with a surrogate mass of 20.74 g (0.7 oz) and with less neptunium. To the slurry, 280 µL of 99.6-µCi/mL plutonium, 700 µL of 63.9-µCi/mL americium, 0.6 mL of 0.07-µCi/mL neptunium, and 35 mg (0.001 oz) of uranium oxide, nitrate, and water were added. This material was used for the second attempt at producing WAXFIX-inorganic sludge specimens. Final concentrations were 1,345 nCi/g (22 ppm) of plutonium; 2,157 nCi/g (0.63 ppm) of americium; 2 nCi/g (2.8 ppm) of neptunium; and 800 ppm of uranium.
- Post-ISTD organic sludge surrogate—Organic sludge surrogate that had been previously treated with the ISTD process was supplied by the sponsor. Of this, 100.29 g (3.5 oz) was spiked as an aqueous slurry identically to the soil above. Final concentrations were 1,390 nCi/g (23 ppm) of plutonium; 2,230 nCi/g (0.65 ppm) of americium; 153 nCi/g (211 ppm) of neptunium; and 813 ppm of uranium.

Table L-1. Prepared concentrations of radionuclides in surrogate.

Surrogate	Units	Americium	Uranium	Neptunium	Plutonium
Soil	nCi/g	2,216.00		152.0	1,381.0
	ppm	0.65	808	210.0	22.6
Organic sludge, Batch 1	nCi/g	2,262.00			1,411.0
	ppm	0.66	825		23.1
Organic sludge, Batch 2	nCi/g	2,241.00			1,397.0
	ppm	0.66	817		22.8
Inorganic sludge, Batch 1	nCi/g	2,219.00		152.0	1,383.0
	ppm	0.65	809	210.0	22.6
Inorganic sludge, Batch 2	nCi/g	2,157.00		2.0	1,345.0
	ppm	0.63	800	2.8	22.0
Post-in-situ-thermal-desorption organic sludge	nCi/g	2,230.00		153.0	1,390.0
	ppm	0.65	813	211.0	23.0

Small samples (1–4 g [0.04–0.1 oz]) of surrogate or waste were placed in a quartz boat, which was placed inside the quartz tube of a tube furnace. The furnace was located in a radiologically controlled fume hood. This sample was then heated to the test temperature and held there for 4 hours. Airflow of 10 mL/minute was pulled through the quartz tube by a rototeflex pump during heating, although at high temperatures, flow was sometimes restricted by the evolution of large amounts of volatilized oil from the organic sludge. As sample gas exited the downstream side of the furnace, it passed through a 0.2-µm filter to trap actinides, followed by a mildly basic bubbler solution to trap acidic anions such as nitrate. Samples were held at temperature for 4 hours. Weight loss from heating also was measured as the mass change following temperature treatment.

During the heated run, grab samples of the gas stream were taken at various times using a 10-mL syringe from a septum port on the line between the filter and the bubbler. These samples were analyzed by GC-ECD for organochlorine constituents and compared against a carbon tetrachloride gas standard. A split was also analyzed by TCD for carbon monoxide, carbon dioxide, nitrous oxide, and sulfur dioxide.

Following ISTD testing, samples were subjected to partition coefficient ( $K_d$ ) measurements in an attempt to ascertain whether actinide behavior had changed. A 1-g-to-10-mL sample-to-liquid ratio is typical and was used here for the surrogate soil and inorganic sludge samples. Because of the nature of the organic sludge ash, those masses were determined after the vials were loaded for radiological control reasons, and the sample masses varied from 1 g (0.04 oz). Once the masses were added to the vials, 10 mL (0.3 oz) of simulated groundwater was added, and these were shaken for 24 hours on a wrist action shaker. The composition of the groundwater is given in Table A-1 in Appendix A. Following contact, the tubes were centrifuged, and the liquid was removed and filtered through a 0.45- $\mu$ m Lure-Lok filter and analyzed for uranium, plutonium, neptunium, and americium. Results were corrected for dilution back to 10 mL (0.3 oz). Therefore, each sample has a unique minimum detectable concentration.

The filters downstream of the heated samples were collected and leached with concentrated nitric acid between selected sample runs. This leachate was analyzed for actinides by inductively coupled plasma-mass spectrometry (ICP-MS) to determine if actinides were volatilized during waste heating. Selected bubbler solutions also were analyzed for nitrates using an ion chromatograph (Dionex 2000i) with carbonate/bicarbonate eluent and sulfuric acid suppressor column.

Sample preparation before analysis by ICP-MS consisted of dissolution by sodium peroxide fusion. Approximately 0.25 g (0.009 oz) of sludge was first digested in 2 mL (0.07 oz) of nitric acid and six drops of hydrogen peroxide and taken to dryness. This was then burned on a hot plate at high setting, transferred to an oven, and burned at 500°C (932°F). The resulting ash was fused at 650–700°C (1,202–1,292°F), with 10–15 times the sample mass of sodium peroxide in a zirconium crucible. The cake was then dissolved in approximately 60 mL (2 oz) of pure water and made acidic with 5 mL (0.2 oz) of concentrated nitric acid. Analysis of uranium, plutonium, and neptunium was performed using Thermo Electron X Series ICP-MS. Counts collected at the appropriate masses were compared to known concentration standards of uranium, plutonium, and neptunium. The known uranium concentration standards were prepared gravimetrically from natural uranium oxide, nitrate, and water. The plutonium and neptunium were prepared by dilution from previously existing, aged, nitric-acid stock solutions characterized by gamma counting at the Radiation Measurements Laboratory. These gamma counting results have an estimated error of 3%. Calibration curves containing three to five standards plus a blank were run before each set of samples. Occasional standards were run interspersed among samples during the day to check for instrument response drift; later in the program, the use of internal standards also was instituted. The ICP-MS software calculated sample concentrations based on these calibration curves.

Minimum detectable concentrations were calculated as three times the mean blank value for a run for the metal of interest. This results in variable detection limits, which depend on the instrument performance (dependent on a daily tune-up), water and reagent quality, standards concentration, and probably other unknown factors, for a given run.

Americium-241 measurements were made by gamma counting using the automated ORTEC Changer Labs digital gamma-ray spectrometer with ORTEC GammaVision software. The typical detection limit of <0.003 ppb corresponds to 10.4 pCi/L.

Carbon tetrachloride compositional analysis was performed by GC-ECD using an HP5590 at the Science and Technology Complex. Samples of pre- and post-ISTD composite organic sludge and pre-ISTD surrogate sludge were extracted at a ratio of 0.2–0.5 g (0.007–0.02 oz) to 2 mL (0.07 oz) with

methanol. The samples were then centrifuged, and the liquid was filtered through a 0.45- $\mu\text{m}$  filter. These solutions were then analyzed by GC.

### **L-3. DATA MANAGEMENT, ANALYSIS, AND INTERPRETATION**

This work was conducted to Quality Level 3 (i.e., standard laboratory practices with no specific calibrations to National Bureau of Standards). No chain of custody of samples was maintained; however, unique sample identifiers were used.

Except where noted, tests were in triplicate. Arithmetic means and standard deviations were calculated for all measurements. Based on the small number of replicates (three) and the complexity of the waste systems being studied, a two-tailed student ( $t$ ) with a 95% confidence level was selected for statistical comparison (where appropriate) of the data.

The gas analysis portion of this program experienced many technical and personnel difficulties. These problems are reflected in data quality, and the off-gas data should be considered qualitative, at best.

The ratio of the actinide concentration in the solid phase to the concentration in the liquid phase gives the  $K_d$ . To calculate the  $K_d$ , the microgram of metal in the liquid was subtracted from that of the solid (based on the spiked concentration for surrogates or from the mean result of compositional analyses for waste). This was divided by the sample mass to calculate the postcontact solid-phase concentration. This concentration was divided by the measured liquid concentration. The result is the  $K_d$ , with units of mL/g. The liquid concentrations were generally so small in relation to that found in the solid that it was not necessary to assess postcontact solid concentrations or perform a mass balance.

#### **L-3.1 Results and Conclusions**

Weight loss data are summarized in Figure L-1 (values of individual measurements are provided in Table L-8). As expected, the soil and Pad A nitrate salt samples (see Table A-2 in Appendix A) showed the smallest (<10 wt%) change in mass on heating. These materials contain minimal amounts of organic compounds and water. The inorganic sludge surrogate samples lost about 25% of their original mass. Most of the mass loss occurred at 105°C (221°F); this is not surprising since the material contained no organics and approximately 20 wt% water (see Table A-4 in Appendix A). The organic sludge surrogate contained approximately 50 wt% volatile organic compounds and 29 wt% Texaco Regal oil (see Table A-3 in Appendix A). Overall, the organic sludge surrogate lost more than 60% of its mass, but not until 275°C (527°F). Surprisingly, given the large percentage of volatile organics in the material, only 5% of the initial mass was lost at 105°C (221°F). The mass loss above 50% may represent the loss of the more volatile elements of the Texaco Regal oil.

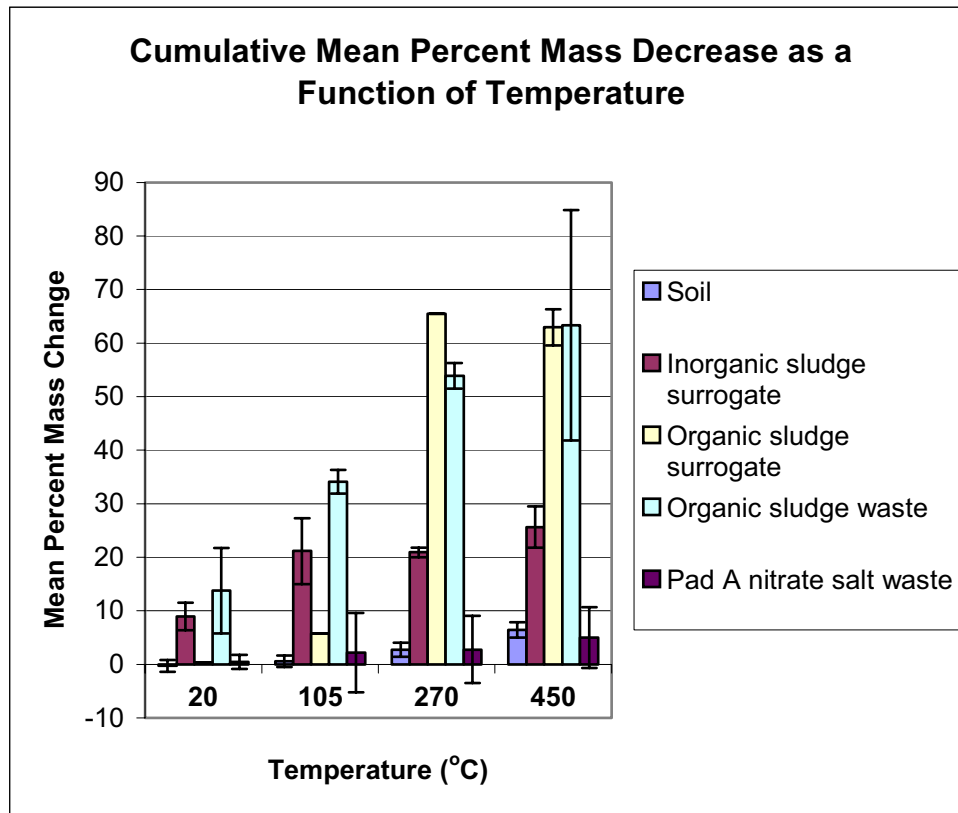


Figure L-1. Cumulative mean percent mass change as a function of temperature.

Grab samples of the gas stream were taken periodically (generally at 0, 1, and 3 hours) during ISTD of the organic sludge surrogate, organic sludge waste, and Pad A nitrate salts from a septum port on the line between the filter and the bubbler. These samples were analyzed by GC-ECD for organochlorine constituents and compared with a carbon tetrachloride gas standard. A split was also analyzed by TCD for carbon monoxide, carbon dioxide, nitrous oxide, and sulfur dioxide. The results are summarized below; the values of the individual measurements are provided in Table L-10.

Organochlorine constituents were analyzed using an ECD. As organic sludge is heated, organic constituents, including organochlorines, would eventually volatilize and then be detectable in the gas stream. The ECD was calibrated using carbon tetrachloride, and in fact, carbon tetrachloride was detected at very low concentrations (ppb levels) in the off-gas, as shown in Figure L-2. Examination of the ECD raw data also showed other peaks in the chromatograms for the organic sludge waste composite caused by additional volatile species with high electron affinity. These are presumably other organochlorine compounds; however, in no organic sludge waste sample (Figure L-3) was a significant amount of carbon tetrachloride found. Examination of the Pad A carbon tetrachloride data in Figure L-4 unexpectedly shows small amounts of carbon tetrachloride (although not the other presumed organochlorines). Therefore, the carbon tetrachloride concentrations reported here for both waste types may be from residual carbon tetrachloride in the system and not from the samples.

Further evidence of this is that no predictable sequence of carbon tetrachloride evolution occurs with time as measurements were made immediately upon achieving temperature for a run, 1 hour into the run and 3 hours into the run. This experimental setup may not have been adequate for collecting the desired off-gas data. The surrogate organic sludge, for which off-gas data are shown in Figure L-2

(only one sample, therefore no confidence interval), were the last data collected and the most reliable data set. The detector and injector were thoroughly cleaned and recalibrated using standards of more appropriate concentration for the expected results. Also, fittings on the off-gas system and sample septum were inspected for leaks and repaired as needed. For these samples, ppm amounts of carbon tetrachloride were evolved from the samples. Surprisingly, these were not seen immediately upon heating but after the samples had baked for 2 or more hours. This suggests that the matrix may have the ability to retain carbon tetrachloride.

If a future off-gas experiment is done, it is recommended that total off-gas for the experiment be collected so that an integrated concentration may be determined. Grab sampling apparently resulted in very low instantaneous concentrations, which could not be related back to the concentrations of these analytes in the original material. Additional problems resulted from the volatilization of oil in the organic sludge samples at temperatures above about 350°C. A large amount of oil deposited throughout the system, even though downstream areas were heat-taped. Further, oil deposited in the injector port and detector on the GC, resulting in large amounts of downtime and probably acting as a source of the residual contamination affecting later samples. In addition, organic sludge begins to lose mass immediately on contact with air. Analytical concentrations thus change with time.

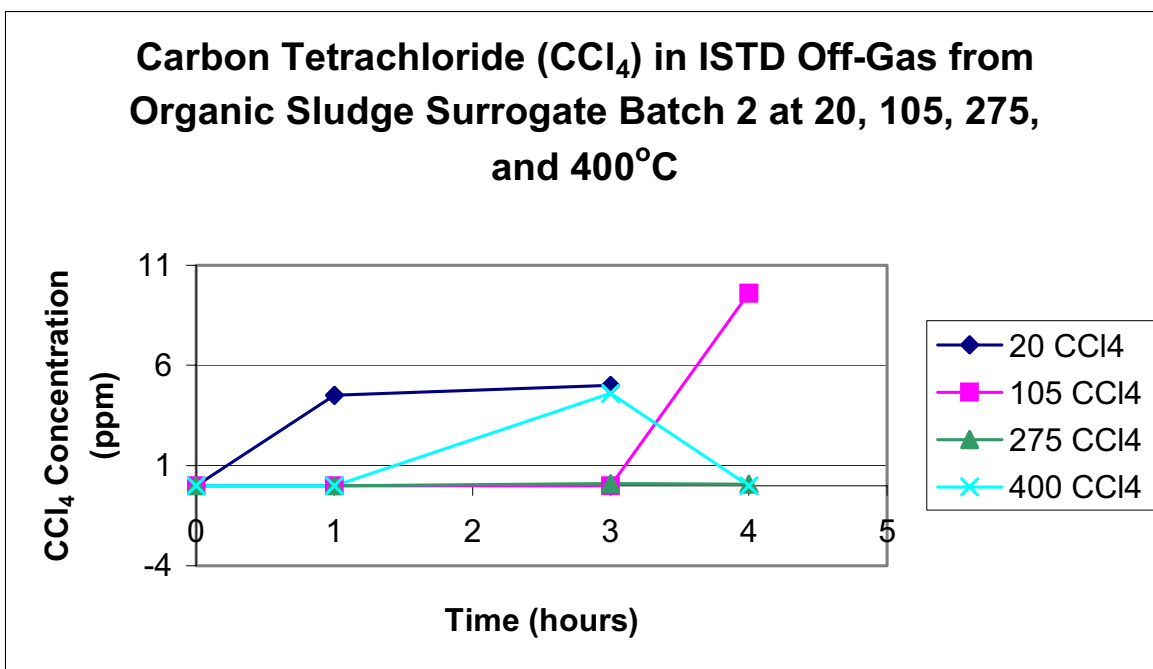


Figure L-2. Carbon tetrachloride concentration in off-gas from in situ thermal desorption as a function of time and temperature for samples of organic sludge surrogate.

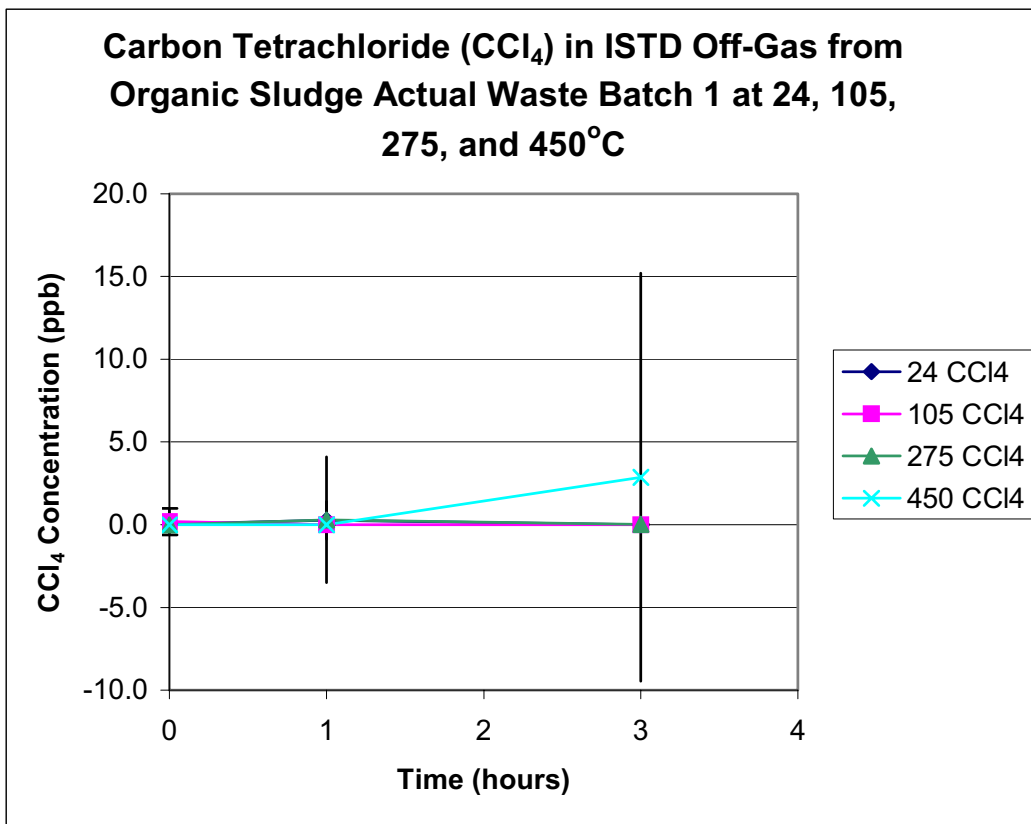


Figure L-3. Carbon tetrachloride concentration in off-gas from in situ thermal desorption as a function of time and temperature for samples of organic sludge waste.

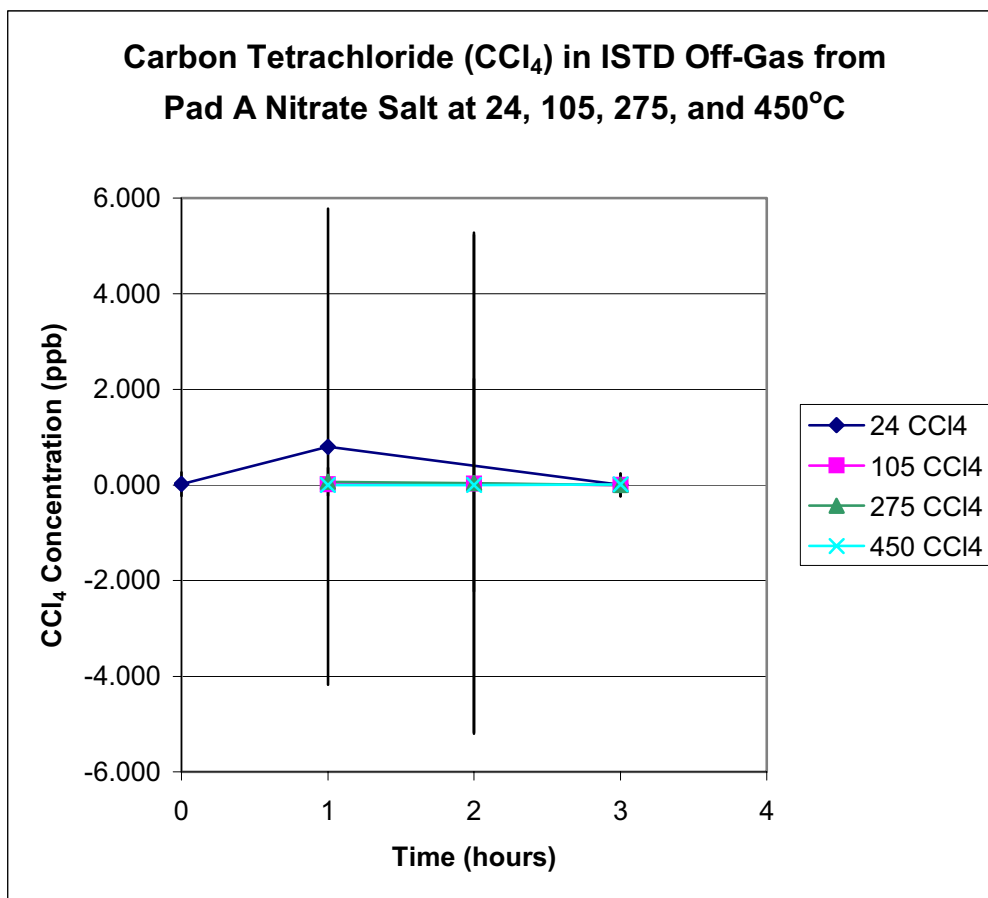


Figure L-4. Carbon tetrachloride concentration in off-gas from in situ thermal desorption as a function of time and temperature for samples of Pad A nitrate salt.

The carbon monoxide, carbon dioxide, nitrous oxide, and sulfur dioxide were analyzed using a TCD detector. Similar problems in experimental design affected quantification of these analytes. In general, no nitrous oxide, carbon monoxide, or sulfur dioxide was detectable in the off-gas of the organic sludge waste composite (Figure L-6), organic sludge surrogate (Figure L-5 [only one sample, therefore no confidence intervals]), and Pad A nitrate salt (Figure L-7) samples, with occasional and apparently random exceptions for the sludge. Only carbon dioxide was routinely detectable, with most samples showing a baseline amount probably from carbon dioxide in the air used as carrier gas. Pure air injections result in similar responses. However, in two of the three organic sludge waste composite samples, runs at 275 and 450°C (527 and 842°F) resulted in a burst of carbon dioxide not detectable after 3 hours. (Values of individual tests are presented in Table L-10.) The surrogate organic sludge sample had similar results at 105, 275, and 400°C (221, 527, and 752°F).

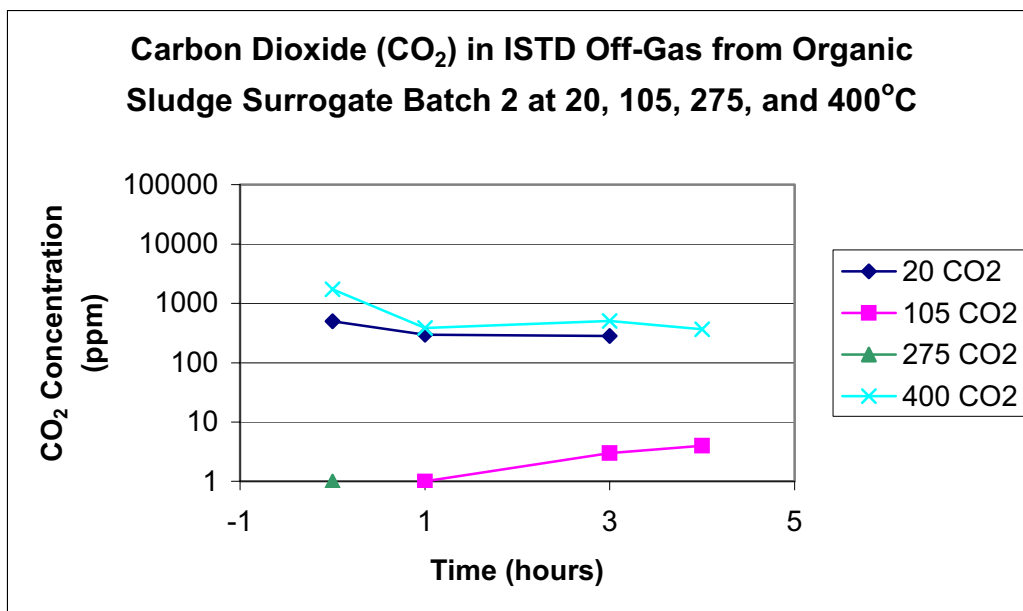


Figure L-5. Carbon dioxide concentration in off-gas from in situ thermal desorption as a function of time and temperature for samples of organic sludge surrogate.

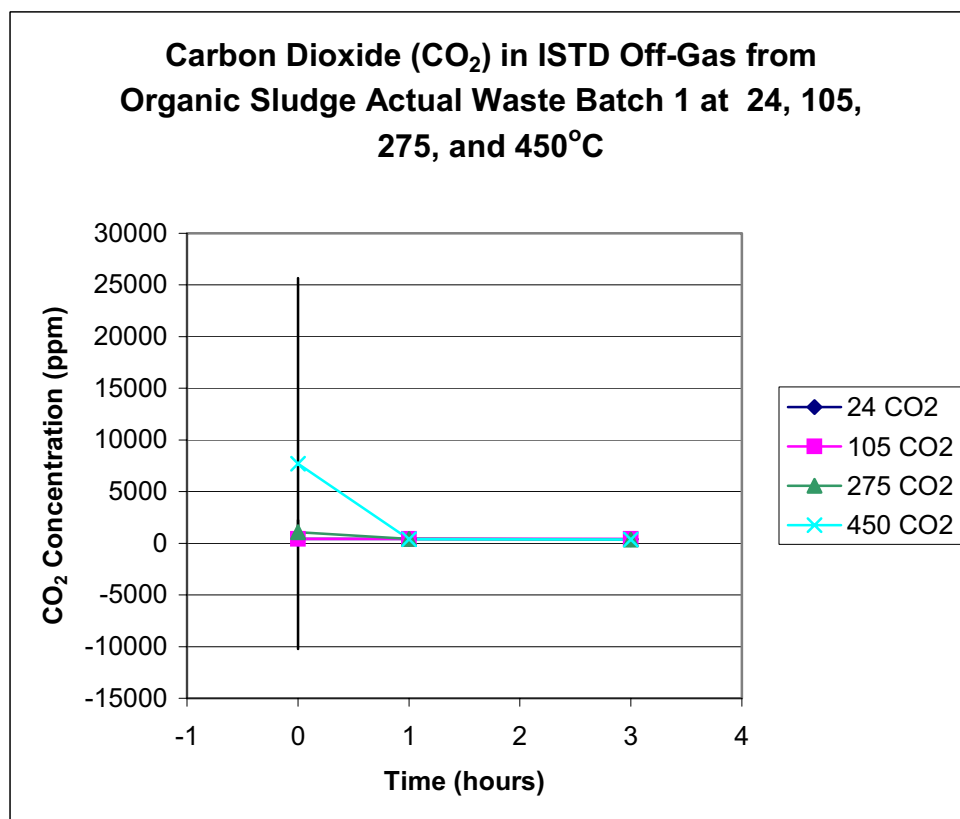


Figure L-6. Carbon dioxide concentration in off-gas from in situ thermal desorption as a function of time and temperature for samples of organic sludge waste.

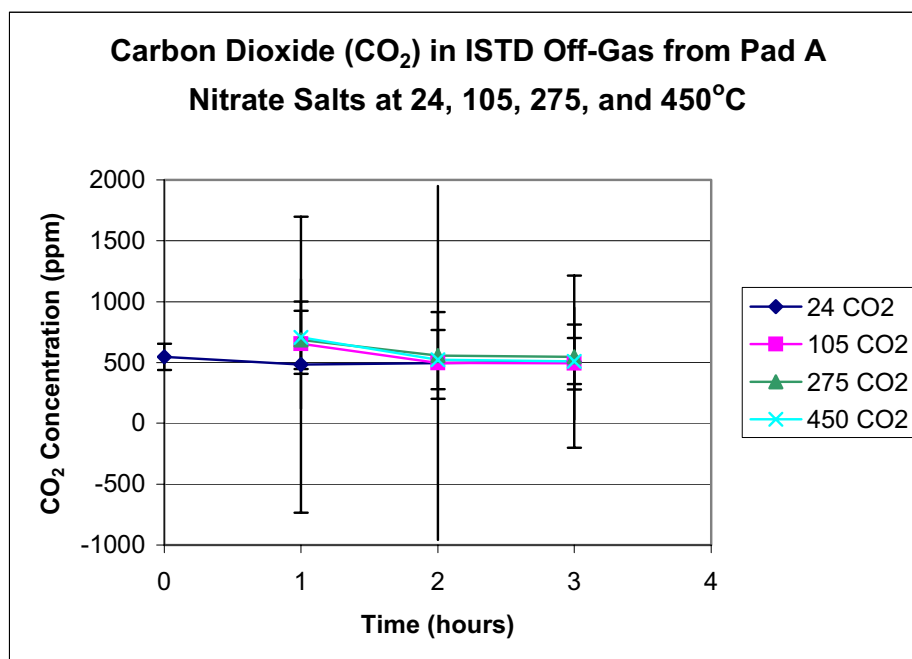


Figure L-7. Carbon dioxide concentration in off-gas from in situ thermal desorption as a function of time and temperature for samples of Pad A nitrate salt.

Figure L-8 shows a summary of the bubbler water analytical results for nitrite and nitrate in off-gas from Pad A salt ISTD and organic sludge waste composite ISTD. (Additional details are available in Table L-15.) Bubbler volume was 100 mL (3.4 oz) initial, made slightly basic with sodium hydroxide. These measurements were made by ion chromatography using an ion chromatograph (Dionex 2000i) with carbonate/bicarbonate eluent and a sulfuric acid suppressor column. No pattern is discernible in the results, and surprisingly, organic sludge waste composite off-gas contained more measurable nitrate than did the Pad A salt. The source of this nitrate is unknown but may be related to system contamination, as previously discussed.

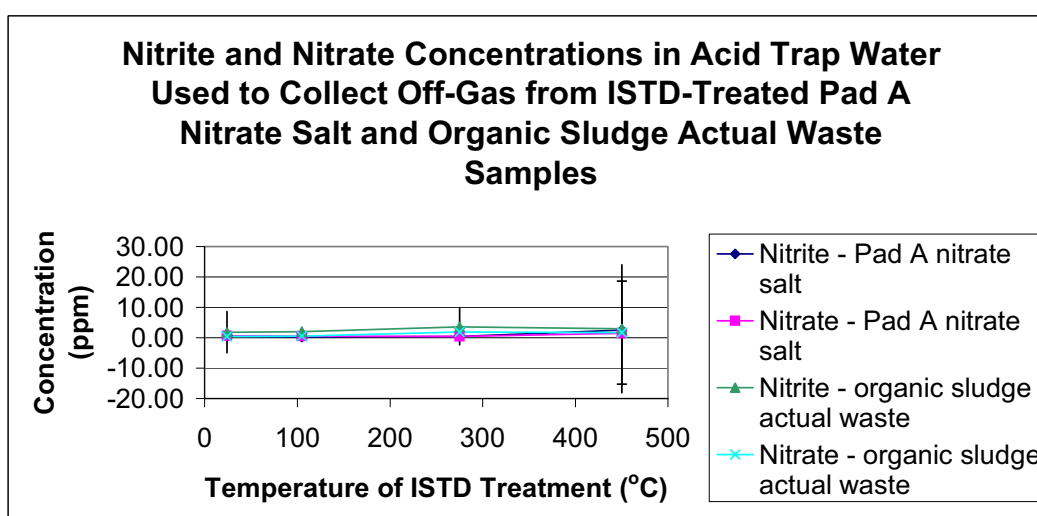


Figure L-8. Nitrite and nitrate concentrations from off-gas in acid trap water for in-situ-thermal-desorption-treated samples of Pad A nitrate salts and organic sludge waste.

A 0.2- $\mu\text{m}$  filter was placed in the off-gas stream to collect any radionuclide particulates released during ISTD treatment. While the present radionuclides—uranium, americium, plutonium, and neptunium—are not normally expected to be “volatile” or to be mobilized by the heating, the presence of chlorinated compounds (such as those compounds present in the organic sludge) has been shown to increase the volatility of some radionuclides. Therefore, the system was monitored for completeness. The results were different than expected, but not conclusive. The filters in the off-gas stream contained uranium during ISTD for soil (see Figure L-9), inorganic sludge surrogate (see Figure L-10), organic sludge surrogate (see Figure L-11), organic sludge waste (see Figure L-12), and Pad A nitrate salt waste (see Figure L-13). For Figures 9–13, 95% confidence intervals are shown; some data points were below detection limits (see Table L-2). The filters for organic sludge surrogate and organic sludge waste contained uranium and plutonium. Most of the measurements of filters showed nondetectable quantities (green shading on Table L-2) of neptunium, americium, and plutonium. No trend in uranium was present on the filter with temperature. Also, the standard deviations and 95% confidence intervals for uranium and plutonium were generally of the same order of magnitude as the means for the uranium and plutonium, suggesting that these data be used more as qualitative rather than quantitative data.

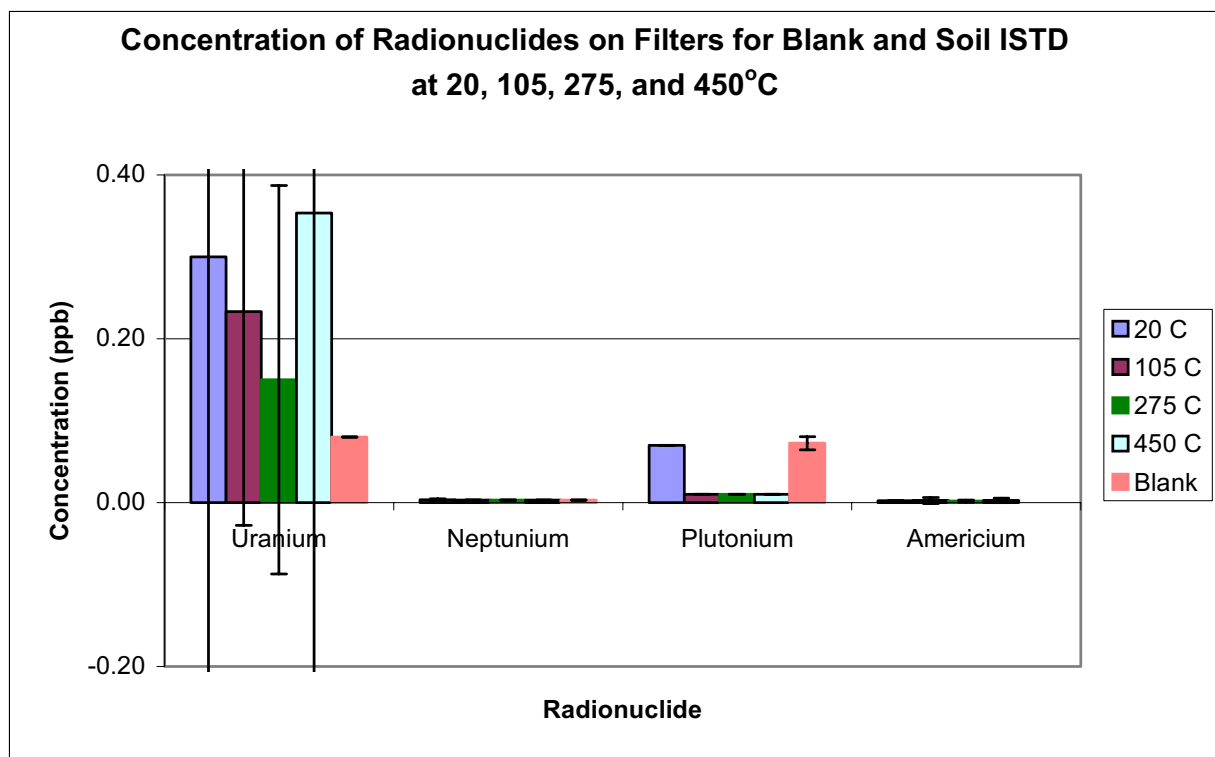


Figure L-9. Concentrations of radionuclides on blank and soil in situ thermal desorption filters.

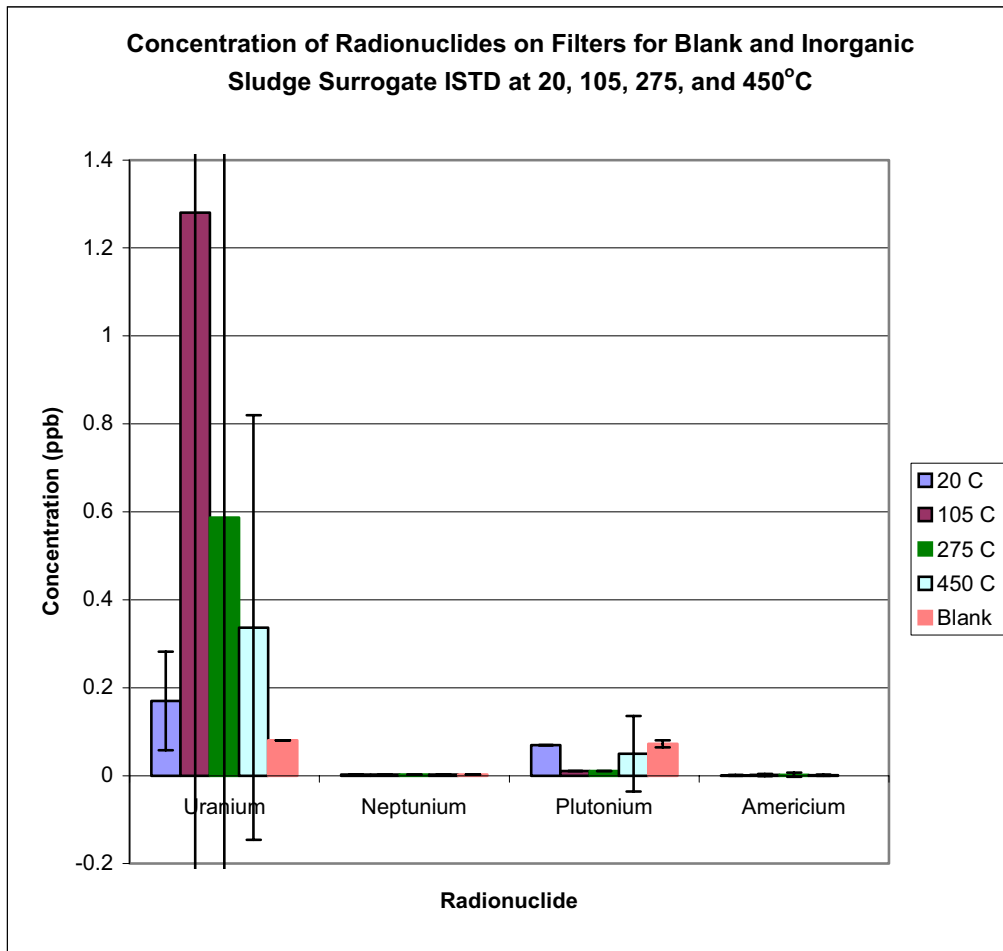


Figure L-10. Concentrations of radionuclides on blank and inorganic sludge surrogate in situ thermal desorption filters.

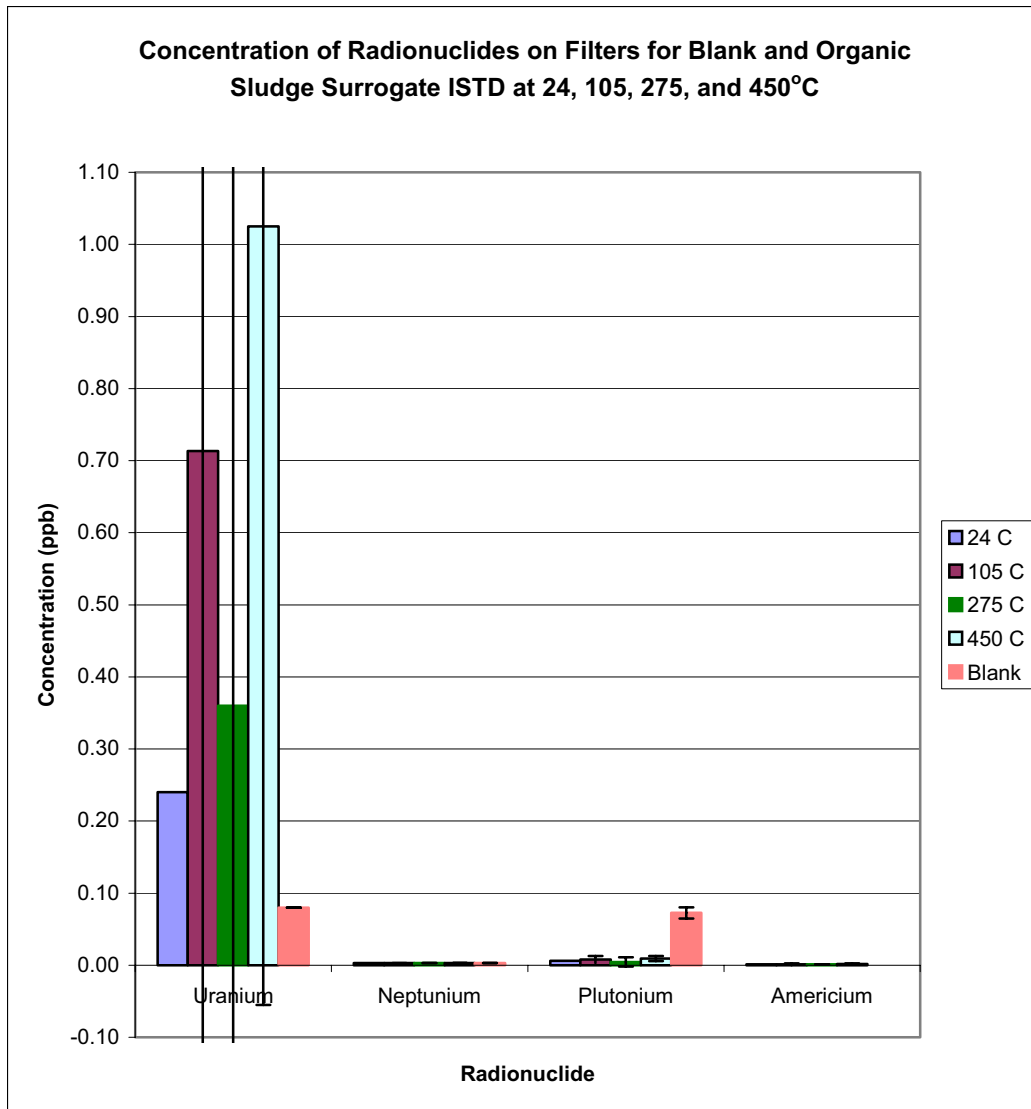


Figure L-11. Concentrations of radionuclides on blank and organic sludge surrogate in situ thermal desorption filters.

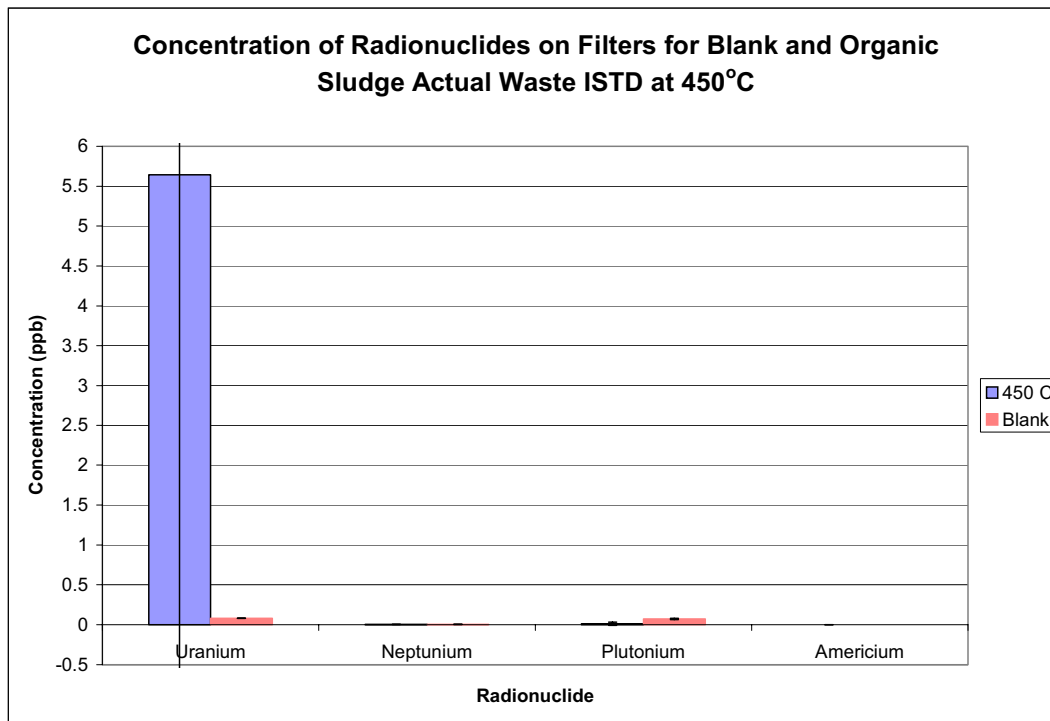


Figure L-12. Concentrations of radionuclides on blank and organic sludge waste in situ thermal desorption filters.

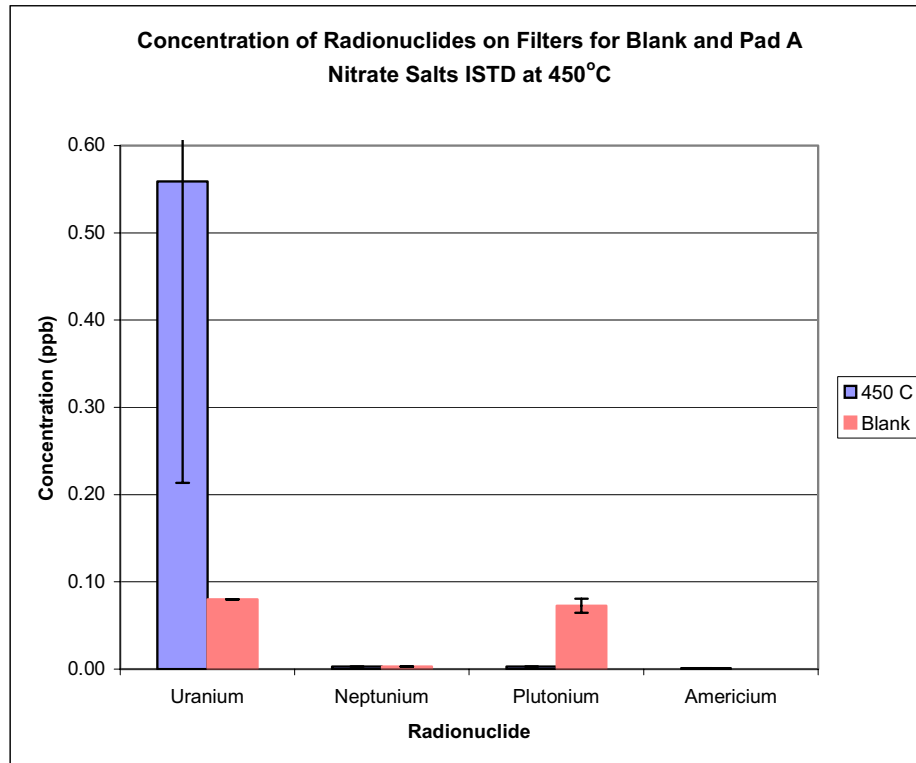


Figure L-13. Concentrations of radionuclides on blank and Pad A waste in situ thermal desorption filters.

Table L-2. Radiological analysis of filters from in situ thermal desorption off-gas stream.

Sample	Temperature (°C)		Americium (ppb)	Uranium (ppb)	Neptunium (ppb)	Plutonium (ppb)
Soil	20	Mean	2.00E-03	3.00E-01	3.33E-03	7.00E-02
		Standard deviation	0.00E+00	2.78E-01	5.77E-04	0.00E+00
		Confidence interval	0.00E+00	6.90E-01	1.43E-03	0.00E+00
	105	Mean	2.67E-03	2.33E-01	3.00E-03	1.00E-02
		Standard deviation	1.53E-03	1.05E-01	0.00E+00	1.65E-10
		Confidence interval	3.79E-03	2.61E-01	0.00E+00	4.09E-10
	275	Mean	1.67E-03	1.50E-01	3.00E-03	1.00E-02
		Standard deviation	5.77E-04	9.54E-02	0.00E+00	1.65E-10
		Confidence interval	1.43E-03	2.37E-01	0.00E+00	4.09E-10
	450	Mean	2.67E-03	3.53E-01	3.00E-03	1.00E-02
		Standard deviation	1.15E-03	3.69E-01	0.00E+00	1.65E-10
		Confidence interval	2.87E-03	9.17E-01	0.00E+00	4.09E-10
Inorganic sludge	20	Mean	1.67E-03	1.23E-01	3.00E-03	7.00E-02
		Standard deviation	5.77E-04	4.51E-02	0.00E+00	0.00E+00
		Confidence interval	1.43E-03	1.12E-01	0.00E+00	0.00E+00
	105	Mean	2.00E-03	1.28E+00	3.00E-03	1.00E-02
		Standard deviation	1.00E-03	1.39E+00	0.00E+00	1.65E-10
		Confidence interval	2.48E-03	3.46E+00	0.00E+00	4.09E-10
	275	Mean	2.00E-03	5.87E-01	3.00E-03	1.00E-02
		Standard deviation	1.73E-03	5.58E-01	0.00E+00	1.65E-10
		Confidence interval	4.30E-03	1.39E+00	0.00E+00	4.09E-10
	450	Mean	1.33E-03	3.37E-01	3.00E-03	5.00E-02
		Standard deviation	5.77E-04	1.94E-01	0.00E+00	3.46E-02
		Confidence interval	1.43E-03	4.83E-01	0.00E+00	8.61E-02
Organic sludge surrogate	24	Mean	1.00E-03	2.40E-01	3.00E-03	6.00E-03
		Standard deviation	N/A	N/A	N/A	N/A
		Confidence interval	N/A	N/A	N/A	N/A
	105	Mean	1.33E-03	7.13E-01	3.00E-03	8.00E-03
		Standard deviation	5.77E-04	7.97E-01	0.00E+00	2.00E-03
		Confidence interval	1.43E-03	1.98E+00	0.00E+00	4.97E-03
	275	Mean	1.00E-03	3.60E-01	3.00E-03	4.50E-03
		Standard deviation	0	0.11314	0	0.000707
		Confidence interval	0	1.01648	0	0.006353
	450	Mean	1.50E-03	1.03E+00	3.00E-03	9.25E-03
		Standard deviation	5.77E-04	6.79E-01	0.00E+00	2.22E-03
		Confidence interval	9.19E-04	1.08E+00	0.00E+00	3.53E-03
Pad A	450	Mean	1.00E-03	5.59E-01	3.00E-03	3.00E-03
		Standard deviation	0.00E+00	2.17E-01	0.00E+00	0.00E+00
		Confidence interval	0.00E+00	3.45E-01	0.00E+00	0.00E+00

Table L-2. (continued).

Sample	Temperature (°C)		Americium (ppb)	Uranium (ppb)	Neptunium (ppb)	Plutonium (ppb)
Organic sludge real	450	Mean	1.00E-03	5.64E+00	3.00E-03	1.10E-02
		Standard deviation	0	7.60811	0	0.008544
		Confidence interval	0	18.9011	0	0.021226
Green denotes two-thirds or more of the data were nondetect.						

Compositional analyses (radionuclide and organic compounds) for two separately prepared batches of organic sludge waste composite are shown in Table L-3. Given the visual lack of homogeneity of the 46 organic sludge waste composite samples (P9GR01012G–P9GR60012G) supplied to the RTC labs by the project, the agreement between the two composite samples is surprising.

The concentration of radionuclides in each sample was measured before and after ISTD treatment. The data are summarized in Table L-4 (individual values are presented in Table L-18). The expected concentrations of radionuclides in samples after heating were calculated based on the mean measured mass losses of samples of the material and the assumption that no radionuclides were released from the sample during heating. The results are presented in Table L-4. No data were available on inorganic sludge surrogate. The data for organic sludge waste and one of the organic sludge surrogate batches suggest that americium was lost during heating, but not uranium. The data for the Pad A waste suggest that uranium and plutonium were lost during heating. Overall, the data showed quite a bit of variation. In several cases, the measured concentration of radionuclides was greater than the expected concentration.

This difference could be caused by the difference between the actual mass loss in the measured sample and the average mass loss used to calculate the expected concentration or errors in the measured concentration of radionuclides.

Table L-4 shows that the mean actinide concentrations increased by a factor of 1.5–2.5 in the posttreatment organic sludge waste composite, undoubtedly caused by the 50–60% mass loss characteristic of treated organic sludge, as shown in Table L-8. The possible exception was americium, which apparently decreased in concentration following heat treatment in the second trial. However, americium was not detectable on gas stream filters (see Table L-2) or in the bubbler solution. The mean concentration of uranium decreased substantially in posttreatment Pad A salt. This uranium also did not appear on the filter downstream of the heated sample or in the bubbler solution, and thus, it must be hypothesized that the uranium or americium or both plated out on the quartz tubing immediately outside the furnace before reaching the filter. Although it was heat taped, visual amounts of organic material also plated there.

Compositional carbon tetrachloride analytical results for organic sludge waste composite also are reported in Table L-3. Pre- and post-ISTD samples showed only trace, or nondetectable, carbon tetrachloride. However, these results are unlikely to reflect the actual carbon tetrachloride concentration. The methanol extraction did not recover large amounts of carbon tetrachloride, again suggesting that the matrix has an unexpected affinity for retention of that compound.

Table L-3. Compositional analysis (radionuclide and organic compounds) for two separately prepared batches of organic sludge waste composite.

Material	Sample	Concentration of Carbon Tetrachloride measured (µg/kg)	Concentration of Carbon Tetrachloride used for calculation (µg/kg)
Organic sludge composite, Batch 1, pre-ISTD	1	Nondetect	0
	2	Trace	0
	3	20	20.0
	Mean		6.7
	Standard deviation		11.5
	Confidence interval		28.7
Organic sludge composite, Batch 1, post-ISTD	1	Trace	0
	2	Nondetect	0
	3	Trace	0
	Mean		0
	Standard deviation		0
	Confidence interval		0
Surrogate Organic Sludge, Batch 2, pre-ISTD	1	Trace	0
	2	14	14.0
	3	32	32.0
	Mean		15.3
	Standard deviation		16.0
	Confidence interval		39.9

ISTD = in situ thermal desorption

Table L-4. Measured and expected concentrations of radionuclides in in-situ-thermal-desorption-treated samples.

Americium					Uranium				Neptunium				Plutonium			
Waste Type	Measured Pre-ISTD	Measured Post-ISTD	Expected Post-ISTD	% Loss	Measured Pre-ISTD	Measured Post-ISTD	Expected Post-ISTD	% Loss	Measured Pre-ISTD	Measured Post-ISTD	Expected Post-ISTD	% Loss	Measured Pre-ISTD	Measured Post-ISTD	Expected Post-ISTD	% Loss
Pad A Salt	9.00E-03	5.00E-02	9.47E-03	-428	2.27E+05	7.54E+03	2.39E+05	97	3.30E-01	1.07E+00	3.47E-01		2.10E+01	2.05E+00	8.00E+00	74
Standard deviation	N/A	4.04E-02	9.97E-05		N/A	5.80E+03	2.51E+03		N/A	1.59E-01	3.66E-03		N/A	4.83E-01	8.42E-02	
Confidence interval	N/A	1.00E-01	2.48E-04		N/A	1.44E+04	6.24E+03		N/A	3.96E-01	9.08E-03		N/A	1.20E+00	2.09E-01	
Low		-5.04E-02	9.23E-03			-6.86E+03	2.32E+05			6.74E-01	3.38E-01			8.51E-01	7.79E+00	
High		1.50E-01	9.72E-03			2.19E+04	2.45E+05			1.47E+00	3.56E-01			3.25E+00	8.21E+00	
Organic sludge surrogate	6.60E+02	5.51E+02	1.74E+03	68	8.E+05	3.20E+06	2.00E+06	-60	N/A	N/A	N/A	N/A	2.E+04	2.60E+05	6.00E+04	-333
Standard deviation	N/A	1.10E+01	4.57E+01		N/A	1.51E+05	5.66E+04		N/A	N/A	N/A		N/A	1.54E+03	1.58E+03	
Confidence interval	N/A	2.74E+01	1.14E+02		N/A	3.76E+05	1.41E+05		N/A				N/A	3.82E+03	3.92E+03	
Low		5.24E+02	1.62E+03			2.82E+06	1.86E+06			N/A	N/A			2.56E+05	5.61E+04	
High		5.78E+02	1.85E+03			3.58E+06	2.14E+06			N/A	N/A			2.64E+05	6.39E+04	
Organic sludge waste, Batch 2	5.80E+02	1.15E+02	1.26E+03	91	1.12E+05	2.25E+05	2.43E+05	7	5.32E+00	3.78E+02	1.16E+01	-3168	1.34E+03	3.41E+03	2.92E+03	-17
Standard deviation	1.63E+02	4.33E+01	3.63E+02		8.44E+03	3.68E+04	2.42E+04		1.08E+00	3.36E+01	2.46E+00		1.04E+02	3.62E+02	2.95E+02	
Confidence interval	4.05E+02	1.07E+02	9.03E+02		2.10E+04	9.14E+04	6.02E+04		2.67E+00	8.36E+01	6.11E+00		2.58E+02	9.00E+02	7.33E+02	
Low		7.55E+00	3.58E+02			1.34E+05	1.82E+05			2.94E+02	5.46E+00			2.51E+03	2.18E+03	
High		2.22E+02	2.16E+03			3.16E+05	3.03E+05			4.62E+02	1.77E+01			4.31E+03	3.65E+03	
Organic sludge waste, Batch 1	3.77E+02	3.77E+02	5.74E+02	34	2.40E+05	2.40E+05	3.36E+05	29	5.09E+00	5.09E+00	1.47E+01	65	4.07E+03	4.07E+03	3.61E+03	-13
Standard deviation	8.31E+01	8.31E+01	3.83E+02		2.59E+04	2.59E+04	1.17E+05		3.21E-01	3.21E-01	5.62E+00		4.33E+02	4.33E+02	9.73E+02	
Confidence interval	2.06E+02	2.06E+02	9.51E+02		6.44E+04	6.44E+04	2.90E+05		7.97E-01	7.97E-01	1.40E+01		1.08E+03	1.08E+03	2.42E+03	
Low		1.71E+02	-3.77E+02			1.76E+05	4.61E+04			4.29E+00	7.23E-01			2.99E+03	1.20E+03	
High		5.83E+02	1.52E+03			3.04E+05	6.27E+05			5.89E+00	2.87E+01			5.14E+03	6.03E+03	

Green denotes two-third or more of the data was nondetect.  
Yellow denotes statistical difference.  
ISTD = in situ thermal desorption

The filter and composition data are not consistent with respect to release of radionuclides during ISTD. Uranium and plutonium are seen on the filters for several waste materials, while americium apparently decreased in organic sludge surrogate and waste samples during heating. In all cases, the 95% confidence intervals are the same order of magnitude or larger than the mean values. Given the inconsistent picture presented by the data, conclusions about the fate of radionuclides during ISTD treatment cannot be made. Additional testing and controls (including a detailed full mass balance) would be needed to confirm the extent of potential radionuclide release during ISTD.

The values for the postcontact analytical metal concentrations and the resulting  $K_d$ s were not normalized for the variable mass leached. The individual measurements are presented in Table L-13; the results are summarized in the figures and tables that follow.

For soil from the Idaho National Laboratory Site spiked with radionuclides and processed by ISTD, the  $K_d$  for americium, uranium, plutonium, and neptunium did not change significantly (compared to pre-ISTD) with temperature, except for americium at 450°C (842°F), where the  $K_d$  increased (see Figure L-14 and Table L-5).

For radionuclide-spiked inorganic sludge surrogate, the  $K_d$ s for americium and plutonium did not change with temperature (see Figure L-15 and Table L-6). The  $K_d$ s for uranium were statistically higher (confidence interval) from pre-ISTD for 275 and 450°C (527 and 842°F), but there was no statistical significant difference between 275 and 450°C (527 and 842°F). The  $K_d$ s for neptunium at 275 and 450°C (527 and 842°F) were statistically lower (confidence interval) than for pre-ISTD, and the  $K_d$  at 450°C (842°F) was statistically lower than the  $K_d$  at 275°C (527°F).

The  $K_d$  measurements shown in Figure L-16 and Table L-9 reveal that surrogate organic sludge did not behave identically to the real waste. The  $K_d$ s for uranium and plutonium were much lower in the surrogate, indicating that more uranium and plutonium leached out of the surrogate during simulated groundwater contact than in the waste. The long duration of contact for the waste may have resulted in the transition of uranium and plutonium to a more refractory form, or the form of uranium and plutonium in the waste may be different than that used to make the surrogate. Heating both the surrogate and real sludge during ISTD treatment appears to have resulted in a less-leachable matrix for uranium, neptunium, and plutonium (trends were consistent, but all differences were not statistically significant), but not americium. However, caution is advised in interpreting the results. All metal concentrations in the aqueous phase were low. Small percent variances in these results near detection limit lead to large changes in  $K_d$ .

Except for the organic sludge samples, ISTD alone did not reduce the mobility (i.e., increase the  $K_d$ ) of uranium, plutonium, neptunium, and americium. In spiked soil, the mobility of neptunium increased with ISTD treatment, the reason for this is not known, but points to the complexities of the system being studied. ISTD did reduce the mobility of uranium, plutonium, and neptunium in organic sludge surrogate and waste when ISTD was performed at high temperatures (i.e., 450°C). This suggests that high-temperature ISTD might be appropriate for use in regions containing high concentrations of organic compounds, but do not contain any compounds that could result in undesired reactions at higher temperatures. In the field, the heterogeneous nature of most waste sites and the relatively high temperature required (450°C) may make high-temperature ISTD impractical from a safety (see discussion in Appendix J) and economics perspective. High-temperature thermal desorption ex situ may still be practical for these wastes. Low-temperature ISTD can remove volatile and semivolatile organic compounds

In the SDA, given the diversity of waste types, the reactivity of some waste combinations at higher temperatures (specifically nitrate salts and some forms of carbon, as discussed in Appendix J), the mixed

nature of the placement of the waste types, and the high temperatures required to reduce radionuclide mobility, ISTD is not practical. Low-temperature (i.e., 150°C) ISTD could still remove volatile and some semivolatile organic compounds, which would aid in subsequent grouting, but the economics of a low-temperature process would have to be explored.

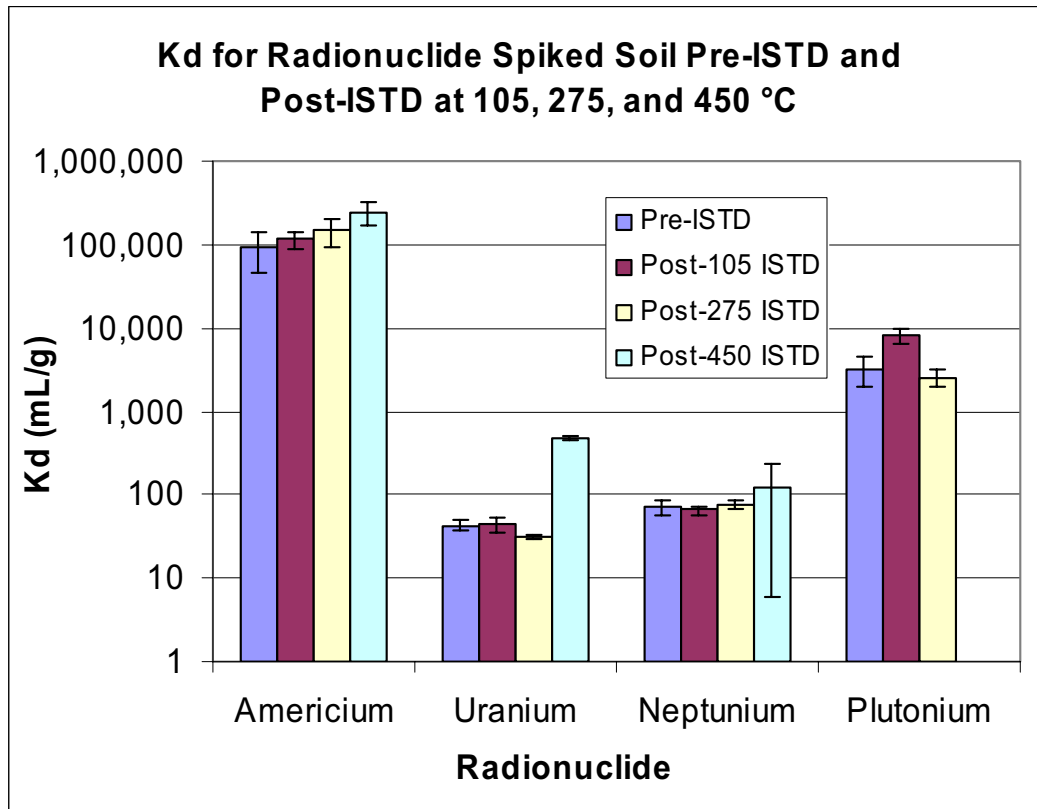


Figure L-14. Partition coefficient for radionuclide spiked soil pre-in-situ-thermal-desorption (20°C) and post-in-situ-thermal-desorption at three temperatures.

Table L-5. Partition coefficient for radionuclide spiked soil pre-in-situ-thermal-desorption (20°C) and post-in-situ-thermal-desorption at three temperatures.

Temperature (°C)	K <sub>dAm</sub> Mean (mL/g)	Standard Deviation	Confidence Interval	K <sub>dU</sub> Mean (mL/g)	Standard Deviation	Confidence Interval	K <sub>dNp</sub> Mean (mL/g)	Standard Deviation	Confidence Interval	K <sub>dPu</sub> Mean (mL/g)	Standard Deviation	Confidence Interval
20	95,366	49,989	124,190	43.1	6.2	15.3	70.6	12.6	31.2	3,196	1,230	3,057
105	116,232	28,169	69,982	44.9	9.7	24.0	65.6	8.0	19.8	8,159	1,812	4,501
275	148,044	52,572	130,607	30.6	1.6	3.9	75.5	9.9	24.6	2,548	554	1,376
450	243,163	74,300	184,585	89.5	20.4	50.7	479.3	114.3	283.9	120	38	94

Green denotes two-thirds or more of the data were nondetect.  
K<sub>d</sub> = partition coefficient

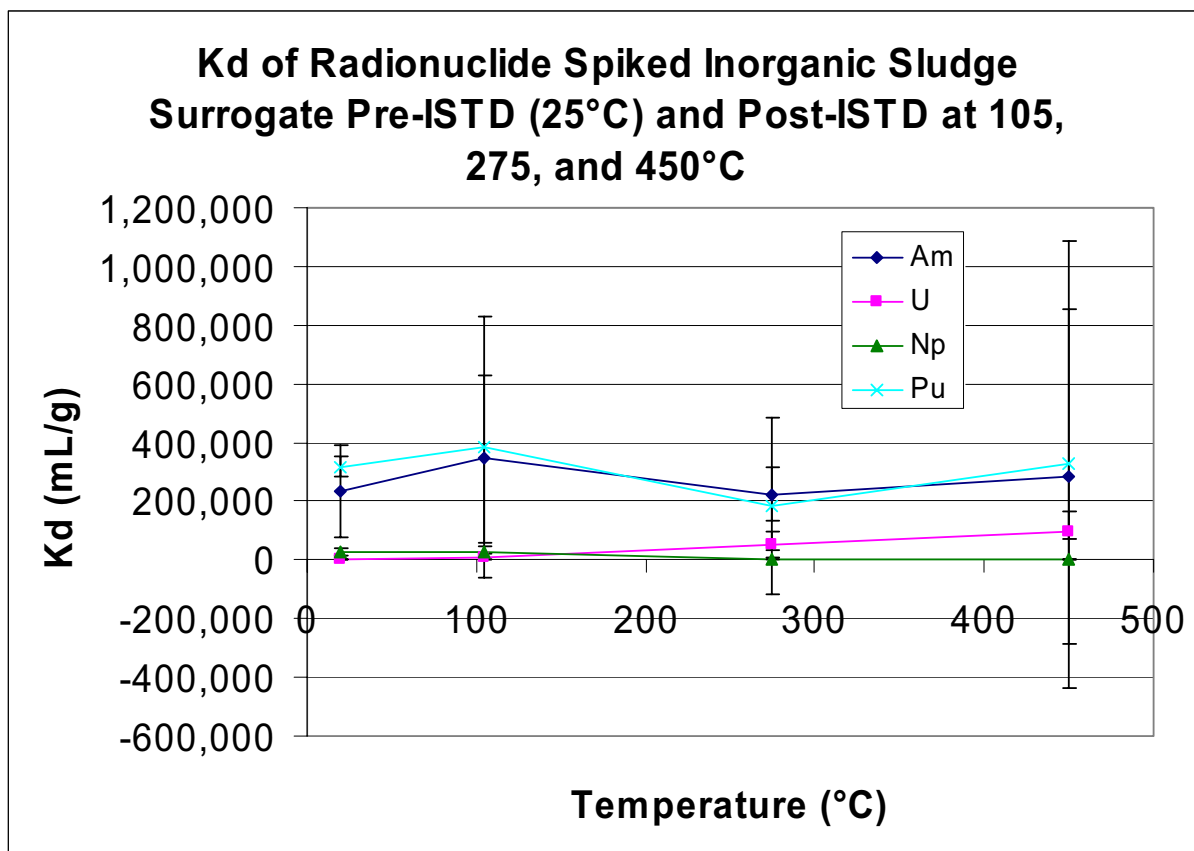


Figure L-15. Partition coefficient for radionuclide spiked inorganic sludge surrogate pre-in-situ-thermal-desorption (20°C [68°F]) and post-in-situ-thermal-desorption at three temperatures.

Table L-6. Partition coefficient for radionuclide spiked inorganic sludge surrogate pre-in-situ-thermal-desorption (20°C [68°F]) and post-in-situ-thermal-desorption at three temperatures.

Temperature (°C)	K <sub>dAm</sub> Mean (mL/g)	Standard Deviation	Confidence Interval	K <sub>dU</sub> Mean (mL/g)	Standard Deviation	Confidence Interval	K <sub>dNp</sub> Mean (mL/g)	Standard Deviation	Confidence Interval	K <sub>dPu</sub> Mean (mL/g)	Standard Deviation	Confidence Interval
20	235,872	63,172	156,941	101	29	73	27,098	4,150	10,310	317,360	13,885	34,496
105	345,132	115,112	285,977	8,166	6,167	15,321	24,138	9,904	24,605	384,756	179,631	446,263
275	224,315	36,242	90,037	52,492	17,777	44,165	4,154	559	1,388	184,003	121,149	300,976
450	287,018	229,651	570,532	96,531	27,234	67,658	32	20	50	326,974	307,205	763,201

Green denotes two-thirds or more of the data were nondetect.  
K<sub>d</sub> = partition coefficient

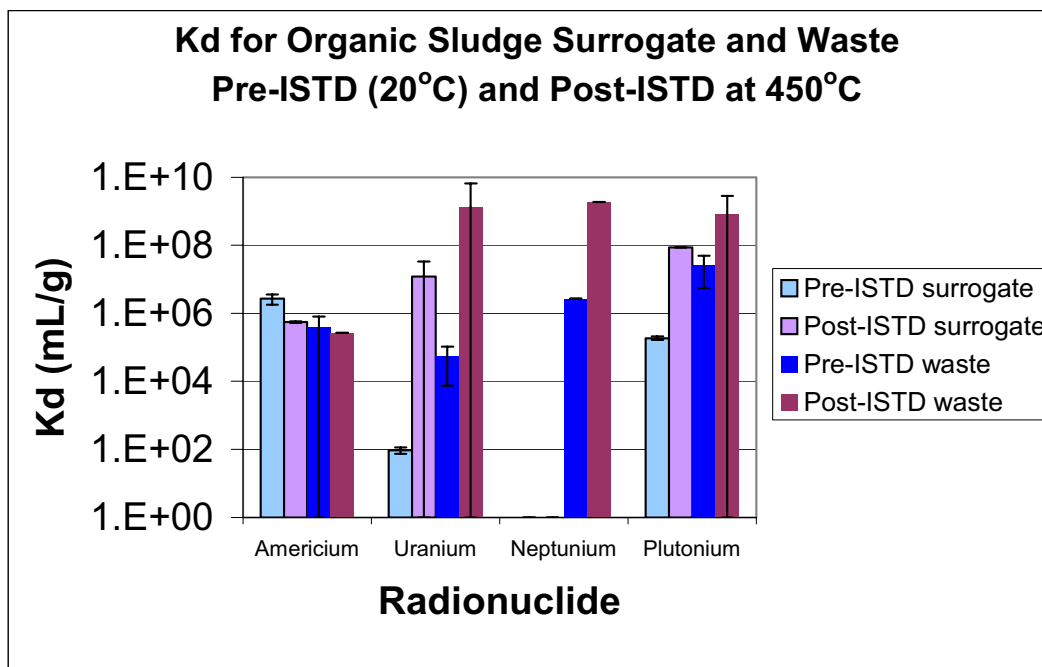


Figure L-16. Partition coefficients for radionuclides in organic sludge surrogate (no neptunium added) and organic sludge waste pre-in-situ-thermal-desorption (20°C [68°F]) and post-in-situ-thermal-desorption (450°C [842°F]).

Table L-7. Partition coefficients for radionuclide organic sludge surrogate (no neptunium added) and organic sludge waste pre-in-situ-thermal-desorption (20°C [68°F]) and post-in-situ-thermal-desorption (450°C [842°F]).

Radionuclide	Temperature (°C)	Surrogate			Waste		
		Mean $K_d$ (mL/g)	Standard Deviation	Confidence Interval	Mean $K_d$ (mL/g)	Standard Deviation	Confidence Interval
Americium	20	2.68E+06	3.45E+05	8.57E+05	3.87E+05	1.67E+05	4.16E+05
	450	5.51E+05	1.11E+04	2.76E+04	2.64E+05	0.00E+00	0.00E+00
Uranium	20	9.33E+01	7.76E+00	1.93E+01	5.58E+04	1.94E+04	4.83E+04
	450	1.21E+07	8.58E+06	2.13E+07	1.36E+09	2.12E+09	5.26E+09
Neptunium	20	N/A	N/A	N/A	2.70E+06	0.00E+00	0.00E+00
	450	N/A	N/A	N/A	1.90E+09	0.00E+00	0.00E+00
Plutonium	20	1.87E+05	9.72E+03	2.42E+04	2.70E+07	8.66E+06	2.15E+07
	450	8.68E+07	0.00E+00	0.00E+00	8.10E+08	7.98E+08	1.98E+09

$K_d$  = partition coefficient

## L-4. VALUES OF INDIVIDUAL MEASUREMENTS

Note that for soil and inorganic sludge surrogates, individual samples were run for each treatment temperature. A fresh sample was used at the beginning of each run, and a weight change recorded for a higher temperature would include any mass that would have been lost at a lower temperature. These data are termed cumulative weight loss in Table L-8. The organic waste, organic sludge surrogate, and Pad A

nitrate salt samples were run differently, in that individual samples were run through the entire heating sequence with weight loss measurements made in between the different temperatures. Weight loss at high temperatures represents only that lost from incremental temperature increase. These data are termed “incremental mass loss” in Table L-9. To be directly comparable to the individual results, the mass lost at lower temperatures should be summed with that lost at the higher temperatures. Total mass losses for the entire temperature sequence for waste samples also are given in Table L-8.

Table L-8. In situ thermal desorption cumulative weight loss on heating.

Sample*	Initial Mass (g)	Post Mass (g)	$\Delta$ (g)
Surrogate Soil			
1-20	1.304	1.301	-0.003
2-20	1.508	1.515	+0.007
3-20	1.230	1.237	+0.007
1-105	0.923	0.914	-0.009
2-105	1.042	1.036	-0.006
3-105	0.958	0.957	-0.001
1-270	0.978	0.948	-0.030
2-270	0.941	0.921	-0.020
3-270	0.950	0.921	-0.029
1-450	0.988	0.920	-0.068
2-450	1.004	0.946	-0.058
3-450	1.082	1.010	-0.072
NOTE: Color of soil gradually changes from tan to orange to reddish brown upon heating.			
Surrogate Inorganic Sludge			
1-20	1.113	1.003	-0.110
2-20	1.297	1.180	-0.117
3-20	1.237	1.140	-0.097
1-105	1.015	0.782	-0.233
2-105	0.994	0.773	-0.221
3-105	1.172	0.957	-0.215
1-270	0.930	0.732	-0.198
2-270	1.074	0.853	-0.221
3-270	1.131	0.895	-0.236
1-450	1.170	0.878	-0.292
2-450	1.158	0.874	-0.284
3-450	1.190	0.864	-0.326
NOTE: Orange tint appears gradually at higher temperatures.			
*Sample code indicates “number”-“temperature” sampled (hours).			

Table L-9. In situ thermal desorption individual weight loss on heating (incremental and total mass loss shown).

Sample*	Initial Mass (g)	Post Mass (g)	$\Delta$ (g)
Organic Sludge Surrogate			
4-20	2.029	2.023	-0.066
4-105	2.023	1.912	-0.111
4-275	1.912	0.700	-1.212
4-450	0.700	0.626	-0.074
Total mass loss			-1.401
A-450	4.025	1.523	-2.502
B-450	4.385	1.744	-2.641
C-450	5.060	1.867	-3.193
D-450	4.806	1.870	-2.936
E-450	4.453	1.695	-2.758
NOTE: Large mass losses were accompanied by oily deposits in furnace tube and on filter at highest temperature treatment. Resultant product is a fine ash.			
Organic Sludge Waste Composite, Batch 1			
1-24	3.697	3.212	-0.485
2-24	4.369	3.894	-0.475
3-24	3.223	2.668	-0.555
1-105	3.212	2.431	-0.781
2-105	3.894	2.920	-0.974
3-105	2.668	2.097	-0.571
1-275	2.431	1.698	-0.733
2-275	2.920	1.980	-0.940
3-275	1.772	1.196	-0.576
1-450	1.698	1.563	-0.135
2-450	1.980	1.797	-0.183
3-450	1.791	1.131	-0.660
Total mass loss 1			2.134
Total mass loss 2			2.572
Total mass loss 3			2.362
NOTE: Samples deposit oil on tube when heated to $\geq 275^{\circ}\text{C}$ .			

Table L-9. (continued).

Sample*	Initial Mass (g)	Post Mass (g)	$\Delta$ (g)
Pad A Samples			
1-24	—	—	—
2-24	—	—	—
3-24	1.492	1.487	-0.005
4-24	1.834	1.824	-0.010
1-105	5.888	5.779	-0.109
2-105	1.124	1.141	+0.017**
3-105	1.487	1.468	-0.019
4-105	1.824	1.783	-0.041
1-275	5.779	5.761	-0.018
2-275	1.141	1.079	-0.062
3-275	1.468	1.458	-0.010
4-275	1.783	1.774	-0.009
1-450	—	—	—
2-450	1.079	1.066	-0.013
3-450	1.458	1.424	-0.034
4-450	1.774	1.734	-0.040
Total mass loss 1			—
Total mass loss 2			—
Total mass loss 3			0.063
Total mass loss 4			0.100
NOTE: Salts melt at temperatures $\geq 275^{\circ}\text{C}$ .			
*Sample code indicates “number”-“temperature” sampled (hours).			
**Sample absorbed moisture from accidental bubbler backflow.			

Table L-10. Gas stream grab sample results.

Sample*	Carbon Tetrachloride (ppb)	Carbon Monoxide (ppm)	Carbon Dioxide (ppm)	Nitrous Oxide (ppm)	Sulfur Dioxide (ppm)
1-24-0	<0.001	<100	495	<100	<100
1-24-1	0.800	<100	443	<100	<100
1-24-3	0.002	<100	447	<100	<100
1-105-0	0.200	<100	471	<100	<100
1-105-1	<0.001	<100	481	<100	<100
1-105-3	<0.001	<100	454	<100	<100
1-275-0	0.007	<100	1,596	<100	<100
1-275-1	0.600	<100	362	<100	<100
1-275-3	0.003	<100	287	<100	<100
1-450-0	0.020	1,093	7,767	<100	<100
1-450-1	<0.001	<100	362	<100	<100
1-450-3	0.002	<100	287	<100	<100
2-24-0	0.100	<100	447	<100	<100
2-24-1	<0.001	<100	495	<100	<100
2-24-3	<0.001	<100	342	<100	<100
2-105-0	0.040	<100	474	<100	<100
2-105-1	<0.001	<100	451	<100	<100
2-105-3	0.008	<100	488	<100	<100
2-275-0	0.020	2,185	917	429	<100
2-275-1	<0.001	1,610	478	645	<100
2-275-3	0.030	820	437	390	<100
2-450-0	0.001	4,772	14,904	<100	<100
2-450-1	<0.001	<100	360	<100	<100
2-450-3	8.600	<100	330	<100	<100
3-24-0	0.100	<100	318	<100	<100
3-24-1	<0.001	<100	372	<100	<100
3-24-3	0.001	<100	342	<100	<100
3-105-0	0.500	383	312	<100	<100
3-105-1	0.002	748	332	<100	<100
3-105-3	0.010	<100	323	<100	<100

Table L-10. (continued).

Sample*	Carbon Tetrachloride (ppb)	Carbon Monoxide (ppm)	Carbon Dioxide (ppm)	Nitrous Oxide (ppm)	Sulfur Dioxide (ppm)
3-275-0	<0.001	<100	675	<100	<100
3-275-1	—	<100	388	<100	<100
3-275-3	<0.001	<100	314	<100	<100
3-450-0	<0.001	<100	454	<100	<100
3-450-1	<0.001	<100	454	<100	<100
3-450-3	<0.001	<100	474	<100	<100

\*Sample code indicates “number”-“temperature”-“time” sampled (hours).

Table L-11. Pad A salt gas stream grab sample results.

Sample*	Carbon Tetrachloride (ppb)	Carbon Monoxide (ppm)	Carbon Dioxide (ppm)	Nitrous Oxide (ppm)	Sulfur Dioxide (ppm)
2-275-0	—	<100	774	<100	<100
2-275-1	—	<100	720	<100	<100
2-275-3	—	<100	669	<100	<100
2-450-0	—	<100	911	<100	<100
2-450-1	—	<100	635	<100	<100
2-450-3	—	<100	597	<100	<100
3-24-0	0.040	<100	536	<100	<100
3-24-1	1.600	<100	485	<100	<100
3-24-3	0.003	<100	512	<100	<100
3-105-0	<0.001	<100	652	<100	<100
3-105-1	0.060	<100	519	<100	<100
3-105-3	0.002	<100	488	<100	<100
3-275-0	0.040	<100	577	<100	<100
3-275-1	<0.001	<100	502	<100	<100
3-275-3	0.002	<100	474	<100	<100
3-450-0	0.010	<100	573	<100	<100
3-450-1	<0.001	<100	481	<100	<100
3-450-3	<0.001	<100	485	<100	<100
4-24-0	0.001	<100	553	<100	<100
4-24-1	<0.001	<100	481	<100	<100
4-24-3	0.004	<100	502	<100	<100

Table L-11. (continued).

Sample*	Carbon Tetrachloride (ppb)	Carbon Monoxide (ppm)	Carbon Dioxide (ppm)	Nitrous Oxide (ppm)	Sulfur Dioxide (ppm)
4-105-0	0.020	<100	652	<100	<100
4-105-1	<0.001	<100	474	<100	<100
4-105-3	0.002	<100	495	<100	<100
4-275-0	0.100	<100	795	<100	<100
4-275-1	0.080	<100	451	<100	<100
4-275-3	0.001	<100	495	<100	<100
4-450-0	—	<100	836	<100	<100
4-450-1	<0.001	<100	454	<100	<100
4-450-3	0.020	<100	451	<100	<100

\*Sample code indicates “number”-“temperature”-“time” sampled (hours).

Table L-12. Organic sludge surrogate, Batch 2.

Sample*	Carbon Tetrachloride (ppb)	Carbon Monoxide (ppm)	Carbon Dioxide (ppm)	Nitrous Oxide (ppm)	Sulfur Dioxide (ppm)
1-20-0	<0.001	<100	498	<100	<100
1-20-0.5	4.500	<100	299	<100	<100
1-20-1	5.000	<100	283	<100	<100
1-105-0	<0.001	<100	817	<100	<100
1-105-1	<0.001	<100	3,628	<100	<100
1-105-3	<0.001	<100	376	<100	<100
1-105-4	9.600	<100	340	<100	<100
1-275-0	<0.001	<100	346	<100	<100
1-275-1	<0.001	<100	703	<100	<100
1-275-3	0.110	<100	877	<100	<100
1-275-4	0.080	<100	780	<100	<100
1-400-0	0.001	<100	1,726	<100	<100
1-400-1	<0.001	<100	385	<100	<100
1-400-3	4.600	<100	509	<100	<100
1-400-4	<0.001	<100	368	<100	<100

\*Sample code indicates “number”-“temperature”-“time” sampled (hours).

Table L-13. Partition coefficient test results.

Sample*	Americium		Uranium		Neptunium		Plutonium	
	(ppb)	(mL/g)	(ppb)	(mL/g)	(ppb)	(mL/g)	(ppb)	(mL/g)
Surrogate soil (soil:water ratio = 1:10) analytical results and partition coefficients								
1-20	<0.006	>137,462	20,470	37.3	3,641	60.7	16.00	1,780
2-20	0.011	40,115	18,540	49.6	3,111	84.7	8.72	3,803
3-20	<0.006	>108,522	17,600	42.5	3,180	66.3	6.65	4,005
1-105	0.006	92,941	10,970	54.6	2,211	72.9	1.89	10,251
2-105	0.006	108,215	14,740	44.8	2,740	66.7	3.16	7,135
3-105	<0.004	>147,541	16,530	35.3	2,881	57.1	2.89	7,091
1-275	0.007	150,134	18,320	31.6	2,393	67.8	10.80	1,924
2-275	0.006	94,458	17,520	31.5	2,017	86.7	6.59	2,982
3-275	0.003	199,540	19,550	28.8	2,380	72.1	7.58	2,737
1-450	0.006	197,374	8,675	75.8	435	430	120	162
2-450	0.003	203,224	8,500	79.8	484	398	178	110
3-450	<0.002	>328,890	6,655	113	343	610	232	88.5
Inorganic sludge surrogate (waste:water ratio = 1:10)								
1-20	0.002	304,910	5,360	135	0.09	31,887	0.07	304,219
2-20	0.004	180,956	9,240	88.0	0.13	24,559	0.08	315,975
3-20	<0.003	221,749	9,250	80.7	0.12	24,847	0.07	331,886
1-105	<0.002	248,527	548	1,144	0.17	12,844	0.09	192,867
2-105	<0.001	472,500	56.3	10,650	0.07	31,343	0.04	412,500
3-105	<0.002	314,370	62.8	12,703	0.01	28,226	0.04	548,900
1-275	<0.002	231,525	14.4	40,826	0.46	4,484	0.16	101,063
2-275	<0.002	256,410	14.9	43,697	0.51	4,469	0.14	127,914
3-275	<0.003	185,010	9.66	72,952	0.70	3,509	0.06	323,033
1-405	<0.002	268,380	6.39	106,658	80.7	29.6	0.07	267,771
2-405	<0.001	525,420	5.69	117,250	43.9	53.2	0.04	659,472
3-405	0.008	67,253	10.4	65,684	177	13.5	0.35	53,680

\*Sample code indicates “number”-“temperature” sampled (hours).

Table L-14. Partition coefficient test results.

Sample	Mass (g)	Americium	Uranium	Neptunium	Plutonium
Pre-ISTD organic sludge surrogate, Batch 2, analytical results (ppb)					
1	1.080	0.27	7,326	0.133	3.552
2	0.874	0.25	8,293	0.126	3.712
3	1.517	0.33	9,720	0.143	3.346
Pre-ISTD organic sludge surrogate, Batch 2, partition coefficients (mL/g)					
1		2.67E+06	102.0	N/A	185,915
2		2.34E+06	87.1	N/A	177,898
3		3.03E+06	90.8	N/A	197,250
Post-ISTD organic sludge surrogate, Batch 2, analytical results (ppb)					
1	0.648	<0.001	1.175	<0.003	0.003
2	0.624	<0.001	0.225	<0.003	<0.003
3	0.648	<0.001	0.164	<0.003	<0.003
Post-ISTD organic sludge surrogate, Batch 2, partition coefficients (mL/g)					
1		539,800	2.72E+06	N/A	86.8E+06
2		549,900	14.2E+06	N/A	>86.8E+06
3		562,000	19.5E+06	N/A	>86.8E+06
Pre-ISTD organic sludge waste composite, Batch 2, analytical results (ppb)					
1	1.168	0.002	2.357	<0.002	0.005
2	0.903	<0.001	1.430	<0.002	0.003
3	1.197	0.002	2.651	<0.002	0.005
Pre-ISTD sludge waste composite, Batch 2, partition coefficients (mL/g)					
1		290,000	47,288	>2.7E+06	2.2E+07
2		>580,000	78,042	>2.7E+06	3.7E+07
3		290,000	42,097	>2.7E+06	2.2E+07
Post-ISTD organic sludge waste composite, Batch 1, analytical results (ppb)					
1	0.662	<0.001	1.276	<0.002	0.006
2	0.809	<0.001	0.059	<0.002	<0.002
3	1.012	0.001	2.622	<0.002	0.022
Post-ISTD organic sludge waste composite, Batch 1, partition coefficients (mL/g)					
1		>264,000	1.8E+08	>1.9E+09	5.7E+08
2		>264,000	3.8E+09	>1.9E+09	>1.7E+09
3		264,000	8.6E+07	>1.9E+09	1.6E+08
ISTD = in situ thermal desorption					

Table L-15. In situ thermal desorption filter blanks.

Sample	Americium (ppb)	Uranium (ppb)	Neptunium (ppb)	Plutonium (ppb)
Blank filter 1	—	<0.08	<0.003	0.08
Blank filter 2	—	<0.08	<0.003	<0.07
Blank filter 3	—	<0.08	<0.003	<0.07
Blank filter 4	—	<0.08	<0.003	<0.07
Mean	—	<0.08	<0.003	<0.07
Standard deviation	—	0.00	0.000	0.00
Confidence interval	—	0.00	0.000	0.01
System blank 1	—	0.25	<0.003	<0.03
System blank 2	—	0.20	<0.003	<0.03
System blank 3	—	0.40	<0.003	<0.03
Mean	—	0.28	<0.003	<0.03
Standard deviation	—	0.10	0.000	0.00
Confidence interval	—	0.26	0.000	0.00

Table L-16. In situ thermal desorption filter actinides.

Sample*	Americium (ppb)	Uranium (ppb)	Neptunium (ppb)	Plutonium (ppb)
Soil				
1-20	<0.002	0.62	0.004	<0.07
2-20	<0.002	0.12	<0.003	<0.07
3-20	<0.002	0.16	<0.003	<0.07
1-105	<0.003	0.23	<0.003	<0.01
2-105	<0.001	0.13	<0.003	<0.01
3-105	0.004	0.34	<0.003	<0.01
1-275	<0.001	0.14	<0.003	<0.01
2-275	<0.002	0.25	<0.003	<0.01
3-275	<0.002	0.06	<0.003	<0.01
1-450	<0.002	0.02	<0.003	<0.01
2-450	0.004	0.75	<0.003	<0.01
3-450	<0.002	0.29	<0.003	<0.01
Inorganic sludge surrogate				
1-20	<0.002	<0.08	<0.003	<0.07
2-20	<0.002	0.12	<0.003	<0.07
3-20	<0.001	0.17	<0.003	<0.07

Table L-16. (continued).

Sample*	Americium (ppb)	Uranium (ppb)	Neptunium (ppb)	Plutonium (ppb)
1-105	<0.001	0.75	<0.003	<0.01
2-105	0.002	0.23	<0.003	<0.01
3-105	0.003	2.86	<0.003	<0.01
1-275	0.004	0.29	<0.003	<0.01
2-275	<0.001	0.24	<0.003	<0.01
3-275	<0.001	1.23	<0.003	<0.01
1-450	<0.001	0.29	<0.003	<0.01
2-450	<0.001	0.55	<0.003	<0.07
3-450	<0.002	0.17	<0.003	<0.07
Organic sludge surrogate, Batch 1				
1-105	<0.002	0.18	<0.003	<0.01
1-450-big	<0.002	0.57	<0.003	<0.01
2-450-big	<0.002	2.01	<0.003	<0.01
Organic sludge surrogate, Batch 2				
3-105	<0.001	1.63	<0.003	0.008
3-275	<0.001	0.28	<0.003	0.004
3-450	<0.001	0.58	<0.003	0.011
4-24	<0.001	0.24	<0.003	0.006
4-105	<0.001	0.33	<0.003	0.006
4-275	<0.001	0.44	<0.003	0.005
4-450	<0.001	0.94	<0.003	0.006
Pad A samples				
1-450	<0.001	0.493	<0.003	<0.003
2-450	<0.001	0.710	<0.003	<0.003
3-450	0.001	0.751	<0.003	<0.003
4-450	<0.001	0.281	<0.003	<0.003
Organic sludge waste composite, Batch 1				
1-450	<0.001	0.666	<0.003	<0.003
Organic sludge waste composite, Batch 2				
2-450	<0.001	1.86	<0.003	0.01
3-450	<0.001	14.4	<0.003	0.02

\*Sample code indicates "number"- "temperature" sampled (hours).

Table L-17. in situ thermal desorption bubbler water analyses.

Sample*	Nitrite (ppm)	Nitrate (ppm)
Pad A salts		
1-24	0.11	0.12
1-105	0.02	Nondetect
1-275	0.34	0.23
1-450	0.84	0.93
2-24	0.11	1.60
2-105	1.01	0.60
2-275	0.34	0.23
3-24	1.69	0.23
3-105	0.03	0.70
3-275	0.79	0.81
3-450	1.80	1.50
4-24	0.11	0.35
4-105	0.02	0.26
4-275	0.14	0.23
4-450	5.18	1.90
Organic sludge waste composite, Batch 1		
1-24	0.24	0.35
1-105	1.58	0.23
1-275	1.58	1.30
1-450	4.73	0.30
2-24	0.23	0.70
2-105	2.65	0.93
2-275	3.04	2.00
2-450	1.24	3.10
3-24	4.96	0.33
3-105	1.80	0.47
3-275	6.31	2.30
*Sample code indicates “number”-“temperature” sampled (hours).		

Table L-18. Compositional analyses for in situ thermal desorption waste.

Sample	Americium-241	Uranium-238	Neptunium-237	Plutonium-239
Organic sludge waste composite, Batch 1, pretreatment (µg/kg)*				
1	67.2	114,325	<9.67	1,175
2	322	214,523	<5.69	1,802
3	403	135,498	<4.92	2,009
Mean	264	154,782	<6.76	1,662
Organic sludge waste composite, Batch 1, posttreatment (µg/kg)				
1	382	263,996	<5.06	4,427
2	292	212,554	<4.78	3,587
3	458	244,108	<5.42	4,189
Mean	377	240,219	<5.09	4,067
Organic sludge waste composite, Batch 2, pretreatment (µg/kg)*				
1	759	102,854	<6.49	1,248
2	441	119,697	<4.37	1,453
3	539	112,346	<5.11	1,322
Mean	580	111,633	<5.32	1,341
Organic sludge waste composite, Batch 2, posttreatment (µg/kg)				
1	68.4	267,576	390	3,241
2	154	203,025	340	3,828
3	122	204,721	404	3,167
Mean	115	225,107	378**	3,412
Pad A salt, pretreatment (µg/kg)				
1	≤0.009	226,710	≤0.33	7.6
Pad A salt, posttreatment (µg/kg)				
1	0.10	4,213	<1.18	2.35
2	<0.03	4,176	<0.89	1.49
3	<0.03	14,238	1.15	2.30
Mean	≤0.02	7,542	≤1.07	2.05
Organic sludge surrogate, Batch 2, pretreatment (from Appendix A) (µg/kg)				
1	660	817,000	N/A	22,800
Organic sludge surrogate, Batch 2, posttreatment (µg/kg)				
1	540	3.32E+06	<0.91	260,536
2	550	3.03E+06	<0.64	258,885
3	562	3.25E+06	<0.79	261,957
Mean	551	3.2E+06	<0.79	260,459

\*These results may be compared with a similar set of analyses reported in Appendix M.

\*\*Although this neptunium value appears to be much higher than the less-than values reported for the other samples, the values before dilution correction were just above the detection limit. There is probably no neptunium present.

Table L-19. Compositional carbon tetrachloride analyses  
for in situ thermal desorption waste.

Sample	Carbon Tetrachloride
Organic sludge waste composite, Batch 1, pretreatment ( $\mu\text{g/kg}$ )	
1	Nondetect
2	Trace
3	20
Organic sludge waste composite, Batch 1, posttreatment ( $\mu\text{g/kg}$ )	
1	Trace
2	Nondetect
3	Trace
Organic sludge surrogate, Batch 2, pretreatment ( $\mu\text{g/kg}$ )	
1	Trace
2	14
3	32

Table L-20. Measured leachate concentrations (ppb) of radionuclides and calculated partition coefficient values for inorganic sludge surrogate.

Sample	Temperature (°C)	Americium (ppb)	K <sub>dAm</sub> (mL/g)	Uranium (ppb)	K <sub>dU</sub> (mL/g)	Neptunium (ppb)	K <sub>dNp</sub> (mL/g)	Plutonium (ppb)	K <sub>dP</sub> (mL/g)
1	20	0.002	3.05E+05	5,360	1.35E+02	0.09	3.19E+04	0.07	3.04E+05
2	20	0.004	1.81E+05	9,240	8.80E+01	0.13	2.46E+04	0.08	3.16E+05
3	20	0.003	2.22E+05	9,250	8.07E+01	0.12	2.48E+04	0.07	3.32E+05
	Mean	0.003	2.36E+05	7,950	1.01E+02	0.11	2.71E+04	0.07	3.17E+05
	Standard deviation	0.001	6.32E+04	2,243	2.95E+01	0.02	4.15E+03	0.01	1.39E+04
	Confidence interval	0.002	1.57E+05	5,572	7.32E+01	0.05	1.03E+04	0.01	3.45E+04
1	105	0.002	2.49E+05	548	1.14E+03	0.17	1.28E+04	0.09	1.93E+05
2	105	0.001	4.73E+05	56.3	1.07E+04	0.07	3.13E+04	0.04	4.13E+05
3	105	0.002	3.14E+05	62.8	1.27E+04	0.01	2.82E+04	0.04	5.49E+05
	Mean	0.002	3.45E+05	222	8.17E+03	0.08	2.41E+04	0.06	3.85E+05
	Standard deviation	0.001	1.15E+05	282	6.17E+03	0.08	9.90E+03	0.03	1.80E+05
	Confidence interval	0.001	2.86E+05	701	1.53E+04	0.20	2.46E+04	0.07	4.46E+05
1	275	0.002	2.32E+05	14.4	4.08E+04	0.46	4.48E+03	0.16	1.01E+05
2	275	0.002	2.56E+05	14.9	4.37E+04	0.51	4.47E+03	0.14	1.28E+05
3	275	0.003	1.85E+05	9.66	7.30E+04	0.7	3.51E+03	0.06	3.23E+05
	Mean	0.002	2.24E+05	13.0	5.25E+04	0.56	4.15E+03	0.12	1.84E+05
	Standard deviation	0.001	3.62E+04	2.9	1.78E+04	0.13	5.59E+02	0.05	1.21E+05
	Confidence interval	0.001	9.00E+04	7.2	4.42E+04	0.31	1.39E+03	0.13	3.01E+05
1	450	0.002	2.68E+05	6.39	1.07E+05	80.7	2.96E+01	0.07	2.68E+05
2	450	0.001	5.25E+05	5.69	1.17E+05	43.9	5.32E+01	0.04	6.59E+05
3	450	0.008	6.73E+04	10.4	6.57E+04	177	1.35E+01	0.35	5.37E+04
	Mean	0.004	2.87E+05	7.5	9.65E+04	101	3.21E+01	0.15	3.27E+05
	Standard deviation	0.004	2.30E+05	2.5	2.72E+04	69	2.00E+01	0.17	3.07E+05
	Confidence interval	0.009	5.71E+05	6.3	6.77E+04	171	4.96E+01	0.42	7.63E+05

Confidence interval = assume 2-tailed student *t* test, n=3 so 2 degrees of freedom, 95% confidence level based on number of samples, *t*<sub>95</sub> = 4.303.  
Green denotes less than detection limit listed, or two-third or more of data was nondetect.  
K<sub>d</sub> = partition coefficient

## **L-5. REFERENCES**

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